Vol. XXVI. [MARCH, 1904.] No. 3.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

ELEVENTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. DETERMINATIONS PUBLISHED DURING 1903.

BY F. W. CLARKE.

Received January 15, 1904.

DURING the year 1903 comparatively few determinations of atomic weight have been published, but some of the work done is of notable importance. Other work is known to be in progress, and the output for the coming year should be of considerable magnitude. The results which have appeared so far are summarized below.

POTASSIUM AND CAESIUM.

The review by Richards and Archibald[1] relates primarily to caesium, but some determinations in regard to potassium were made incidentally. First, potassium chloride, dried at 700°, was precipitated by silver nitrate. The latter had been prepared from a known quantity of pure silver, so that two distinct ratios were determined. Vacuum weights are given throughout, and the reductions were made with Ag = 107.930, and Cl = 35.455. O = 16. For the ratio between KCl and AgCl we have

[1] *Proc. Am. Acad.*, **38**, 443; also *Ztschr. anorg. Chem.*, **34**, 353.

Weight KCl.	Weight AgCl.	Atomic weight K.
2.50019	4.80600	39.137
2.50391	4.81325	39.136

For the ratio Ag: KCl the data are

Weight KCl.	Weight Ag.	Atomic weight K.
2.50019	3.61747	39.140
2.50391	3.62283	39.141

Mean of both series, K = 39.139.

Another set of measurements was made by an entirely new method. Potassium nitrate was ignited with weighed quantities of silica; K_2O as silicate remained, and N_2O_5 (or rather, its decomposition products) was driven off. From the ratio thus ascertained, $K_2O : N_2O_5$, the atomic weight of potassium was calculated, with O = 16 and N = 14.040. The data are as follows:

Weight KNO_3.	N_2O_5 lost.	Atomic weight K.
1.81034	0.96692	39.138
3.14564	1.68005	39.142
2.55598	1.36512	39.142
	Mean,	39.141

For the work on caesium, the material was purified by repeated recrystallization of the dichloriodide, $CsCl_2I$. By heating this salt to from 90° to 100° in an electric oven it was reduced to CsCl, which was spectroscopically free from other alkaline salts. Several samples of chloride were prepared, and several series of determinations were made, similar to the two sets of chloride analyses given under potassium. The data thus obtained are as follows:

RATIO AgCl : CsCl.

First Series.

Weight CsCl.	Weight AgCl.	Atomic weight Cs.
3.83054	3.26240	132.901
3.95120	3.36532	132.892
2.27237	1.93555	132.882
3.02935	2.58003	132.901
3.19774	2.72382	132.878
	Mean,	132.891

Second Series.

2.35068	2.00253	132.858
2.06245	1.75678	132.878
2.56372	2.18358	132.892
	Mean,	132.876

Third Series.

Weight CsCl.	Weight AgCl.	Atomic weight Cs.
2.01881	1.71972	132.868
1.77391	1.51093	132.886
	Mean,	132.877

Fourth Series.

3.08160	2.62484	132.881
3.13117	2.66720	132.872
5.06656	4.31570	132.876
	Mean,	132.876

RATIO Ag : CsCl.

First Series.

Weight CsCl.	Weight Ag.	Atomic weight Cs.
3.83054	2.45600	132.880
3.95120	2.53351	132.871
2.27237	1.45686	132.891
3.02935	1.94244	132.868
3.19774	2.05023	132.883
	Mean,	132.878

Second Series.

2.35068	1.50720	132.876
2.06245	1.32251	132.862
	Mean,	132.869

Third Series.

2.01881	1.29434	132.886
1.77391	1.13743	132.871
	Mean,	132.878

Fourth Series.

3.08160	1.97590	132.872
3.13117	2.00760	132.879
5.06656	3.24850	132.879
	Mean,	132.877

The general mean of these eight means gives Cs = 132.878.

By the ignition of calcium nitrate with silica the following data were obtained:

Weight $CsNO_3$.	N_2O_5 lost.	Atomic weight Cs.
3.76112	1.04273	132.882
5.33334	0.92416	132.876
4.81867	1.33590	132.886
5.04807	1.39960	132.871
	Mean,	132.879

Caesium bromide was also studied by Richards and Archibald, and two ratios are given by them. First, for the ratio CsBr : AgBr. Br = 79.955.

Weight CsBr.	Weight AgBr.	Atomic weight Cs.
3.49820	3.08815	132.878
6.20409	5.47673	132.883
7.17300	6.33213	132.880
	Mean,	132.880

Secondly, for the ratio CsBr : Ag.

Weight CsBr.	Weight Ag.	Atomic weight Cs.
3.49820	1.77402	132.873
6.20409	3.14606	132.885
7.17300	3.63740	132.884
	Mean,	132.881

The final values deduced by the authors from all their data are, with O = 16, K = 39.140, Cs = 132.879.

FLUORINE.

Julius Meyer[1] has redetermined the atomic weight of fluorine by a new and simple method. Calcium oxide was converted into fluoride, with suitable precautions, and from the ratio thus measured the atomic weight of fluorine was easily computed. First, the oxide, slaked with water, was converted by hydrochloric acid into chloride. The latter was then repeatedly evaporated with pure hydrofluoric acid, and the resulting fluoride was ignited to constant weight at a red heat. The data, with vacuum weights, are as follows:

Weight CaO.	Weight CaF_2.	Atomic weight F.
6.1883	8.6215	19.036
4.2736	5.9548	19.042
6.2931	8.7658	19.029
5.7767	8.0485	19.038
4.9836	6.9426	19.033
	Mean,	19.036

Calculated by Meyer with O = 16 and Ca = 40.136.

IRON.

A new determination of the atomic weight of iron, by Baxter,[2] is based upon the analysis of ferrous bromide. This salt was

[1] *Zischr. anorg. Chem.*, **39**, 313.
[2] *Proc. Am. Acad.*, **39**, 245.

sublimed in porcelain tubes, dissolved in acidulated water, oxidized by potassium dichromate, and then mixed with a solution of silver nitrate. The silver bromide was collected on a Gooch filter and weighed. In two experiments the ferrous bromide was also balanced against silver alone. The data, as published, involve a number of corrections, which complicate the table of results. The following corrected weights have kindly been supplied to me by Dr. Baxter. They are reduced to a vacuum, and the calculations represent O = 16, Ag = 107.93, and Br = 79.955.

Weight $FeBr_2$.	Weight AgBr.	Weight Ag.	Atomic weight Fe.
3.55929	6.19873	.....	55.856
3.07448	5.35450	.....	55.852
2.96102	5.15696	.....	55.849
4.00791	6.97983	.....	55.862
2.96102	.....	2.96234	55.854
4.00791	.....	4.00937	55.871
		Mean,	55.857

One correction still remains to be applied. Ferrous bromide, like the corresponding bromides of cobalt and nickel, when sublimed in porcelain, becomes contaminated with small quantities of sodium bromide. In this case the contamination amounted to 0.138 per cent. Corrected for this impurity the final value for Fe becomes 55.871. This agrees fairly well with the value 55.883 previously determined by Richards and Baxter. The number 55.88 is probably quite nearly correct.

As a check upon the accuracy of his work, Dr. Baxter also redetermined the ratio between silver and bromine. In three independent experiments his data are as follows:

Weight Ag.	Weight AgBr.	Ratio Ag : AgBr.
4.77783	8.31754	57.4428
5.87977	10.23533	57.4459
4.82995	8.40809	57.4441
	Mean,	57.4443

This is nearly identical with the mean derived from Stas' experiments, *viz.*, 57.4445. From the two experiments of the ferrous bromide series in which both Ag and AgBr were determined, the values for the ratio became 57.444 and 57.442.

ANTIMONY.

The electrolytic method for determining the atomic weight of

this element has been investigated by Cohen and Strengers.[1] Antimony and silver were thrown down simultaneously in the same circuit, the former from solutions of trichloride. It was found that the atomic weight thus obtained increased with the concentration of the antimony solution, varying from 120.78 to 121.92, when Ag = 107.93. The concentrations varied from 3.3 to 83.3 grams of chloride in 100 grams of solution, and the gain in apparent atomic weight was quite regular. The method, therefore, involves unknown uncertainties, and is not applicable to the purpose of measuring the atomic weight in question.

LANTHANUM.

In the report of this committee for 1902 a set of determinations, by Jones, of the atomic weight of lanthanum was given, and also certain criticisms of the work by Brauner, who claimed that it was vitiated by constant errors. In his reply[2] to Brauner, Jones claims to show that the alleged errors do not exist, and new data are given in corroboration of the former series. In the new work hygroscopic impurity was carefully guarded against, and the lanthanum sulphate was proved to be neutral. Five syntheses of sulphate from oxide, conducted in porcelain crucibles, gave the subjoined results, when O = 16 and S = 32.06.

Weight La_2O_3.	Weight $La_2(SO_4)_3$.	Atomic weight La.
1.2161	2.1132	138.79
1.6311	2.8342	138.81
1.7804	3.0938	138.79
1.4168	2.4619	138.80
1.9702	3.4235	138.80
	Mean,	138.80

The value found in 1902 was La = 138.77.

In these experiments the oxide used was perfectly white. Brauner and Pavliček heated their oxide, not in porcelain, but in platinum crucibles, and found a higher value for the atomic weight, 139.04. Jones now gives the results of two experiments in platinum, and obtains similar values, as follows:

Weight La_2O_3.	Weight $La_2(SO_4)_3$.	Atomic weight La.
1.2820	2.2264	139.02
1.3885	2.4110	139.07

[1] *Proc. Amsterdam Acad.*, **5**, II, 543.
[2] *Ztschr. anorg. Chem.*, **36**, 92.

In this case the oxide was somewhat discolored, and most so near the wall of the platinum crucible. Jones regards this as due to a slight oxidation of the material, which would account for the higher atomic weight. The controversy, however, is probably not yet ended. Determinations of atomic weight by some process radically different from either the sulphate or the oxalate method may be necessary to settle the questions at issue.

CERIUM.

Upon the atomic weight of cerium two important and elaborate memoirs have appeared; one by Brauner and Batěk,[1] the other by Brauner[2] alone. Only the results of the two investigations can be given here; for details, the original publications must be consulted.

First, the salt $Ce_2(SO_4)_3.8H_2O$ was dehydrated by heating to 440°. The *anhydrous* sulphate was then reduced by ignition, with suitable precautions, to Ce_2O_4. In this way, operating upon various fractions of material, Brauner and Batěk found

Weight sulphate.	Weight oxide.	Atomic weight Ce.
1.5074	0.9130	140.12
1.7979	1.08945	140.32
1.5937	0.9665	140.13
2.6240	1.5895	140.18
1.2161	0.7370	140.38
1.4974	0.9130	140.12
1.2192	0.7386	140.21
	Mean,	140.21

Calculated with O = 16, S = 32.06, and reduction to a vacuum.

In the second paper Brauner gives a series of experiments in which the salt $Ce_2(SO_4)_3.8H_2O$ was directly reduced to Ce_2O_4. The data, with vacuum weights throughout, are as follows:

Weight octahydrate.	Weight oxide.	Atomic weight Ce.
1.98989	0.96175	140.26
1.99154	0.96251	140.25
2.33919	1.13027	140.17 (?)
1.95882	0.94679	140.28
1.20961	0.58453	140.21
1.54162	0.74504	140.24
1.67748	0.81074	140.25
2.02736	0.97985	140.26
	Mean,	140.24

[1] *Zischr. anorg. Chem.*, **34**, 103.
[2] *Ibid.*, **34**, 207.

Rejecting the third of these values, in which Brauner suspects a possible loss during the experiment, the mean of the remaining seven becomes 140.25.

For the determinations which the authors carried out by the oxalate method, the data are too complex for full citation here. Only results can be given. The method involves two steps: first, ignition of cerium oxalate to Ce_2O_4; and secondly, determination of C_2O_3 in another portion of oxalate by titration with potassium permanganate. From the ratio between C_2O_3 and Ce_2O_4 the atomic weight of cerium is calculated. By this process Brauner and Batěk made the following eighteen determinations:

140.28	140.075
140.465	140.075
140.45	140.20
140.165	140.10
140.29	140.32
140.43	140.30
140.38	140.37
140.075	140.42
140.33	140.05
Mean,	140.265

One more experiment by this method, cited by Brauner in the second paper, gave Ce = 140.246. As the final result of both investigations, Brauner gives

$$Ce = 140.25.$$

This agrees with earlier work by Brauner, and also with determinations by Robinson, and should replace all other measurements of this atomic weight.

RADIUM.

In the report of this committee for 1902, Madame Curie's determinations of the atomic weight of radium were cited. Her data have since appeared in full,[1] as follows:

Weight $RaCl_2$.	Weight AgCl.	Atomic weight Ra.
0.09192	0.08890	225.3
0.08936	0.08627	225.8
0.08839	0.08589	224.0

Calculated with Ag = 107.8 (?) and Cl = 35.4. Madame Curie regards the value Ra = 225 as correct to within about one unit. This conclusion finds confirmation in the work of W. Marshall

[1] *Ann. chim. phys.*, [7], **30**, 140.

Watts,[1] who has studied relations between the spectra of the elements and the squares of their atomic weights. By comparing the spectra of Ba and Ra he finds Ra = 225.05; and for the spectra of Hg and Ra, Ra = 224.63. Mean of all his observations, Ra = 224.89. Runge and Precht,[2] on the other hand, comparing the spectra of Ca, Sr, Ba and Ra, concluded that the atomic weight of radium is 257.8. The apparent instability of radium offers an argument in favor of this higher value. In a later paper[3] Runge criticizes Watts' method of calculation, and argues that it is entirely fallacious.

MISCELLANEOUS NOTES.

Krypton.—A new determination of the density of krypton, by Ramsay,[4] gives the value 40.81. The atomic weight, therefore, is 80.62.

Bismuth.—Adie,[5] seeking to determine the atomic weight of bismuth, obtained discordant results, which were found to be due to small quantities of silica in the material studied. To this impurity he ascribes the discrepancies between the measurements of previous observers. A preliminary experiment upon pure bismuth gave Bi = 208.8, approximately.

Tellurium.—The atomic weight of tellurium has been discussed by Koethner,[6] by Seubert,[7] and by Pellini.[8] Koethner, from an examination of all the published determinations, concludes that the most probable value is Te = 126.71, when H = 1. Seubert argues in favor of Te = 126.6, or 127.6 with O = 16. Pellini, considering the anomalous position of tellurium in the periodic system, suggests a possible impurity in the form of a radioactive element of higher atomic weight.

Numerical Relations.—This subject is discussed by Mills,[9] under the caption "Numerics of the Elements." An attempt is made to compute the atomic weights from a general mathematical formula, and arguments are adduced to show that the most probable value for O is 15.94 when H = 1. Another paper, by

[1] *Phil. Mag.*, [6], **5**, 203; and (for radium) **6**, 64.
[2] *Physikal. Ztschr.*, **4**, 285.
[3] *Phil. Mag.*, [6], **6**, 698.
[4] *Chem. News*, **87**, 159.
[5] *Proc. Cambridge Phil. Soc.*, **12**, 240.
[6] *Ztschr. anorg. Chem.*, **34**, 403.
[7] *Ibid.*, **35**, 205.
[8] *Gazz. chim. ital.*, **33**, II, 35.
[9] *Phil. Mag.*, [6], **5**, 543.

Hughes,[1] develops relations which suggest that the elements may be constituted analogously to the organic radicals. Still a third paper, by Henry Wilde, also deserves attention.[2]

International Atomic Weights.—The report of the smaller International Committee for 1903[3] has been sharply criticized by Ostwald.[4] To this criticism, which related mainly to the standard of values, Seubert published a reply.[5] The subject of a standard has also been discussed by Winkler,[6] whose paper called forth a rejoinder by Landolt and Ostwald.[7] In a still later note, Winkler answers his critics.[8] For the purposes of this report, these references to literature are sufficient.

THE CHEMICAL COMPOSITION OF COOKED VEGETABLE FOODS.

By Miss Katharine I. Williams.

Received December 9, 1903.

The investigations described in the following pages were undertaken at the suggestion of Sir William Ramsay; during the course of the work I have received much kind assistance from Dr. S. Young, in the way of advice as to working-details. Most of the previous work published on this subject deals with analysis of raw foods; the main object of this investigation was to gain information regarding the composition of foods as served at table.

The fresh, green vegetables were bought when in full season, the leeks in April, the rhubarb in March, the broccoli and Brussels sprouts in January, asparagus in the middle of May, while the green artichokes were purchased in June.

General Preparation of the Samples Used.—The chief consideration was to obtain a sample of each vegetable food as it would be served at table, therefore, in the case of broccoli, Brussels sprouts, rhubarb, leeks, asparagus, and green artichokes the usual

[1] *Chem. News*, **88**, 298.
[2] *Mem. Manchester Lit. Phil. Soc.*, **48**, 1.
[3] This Journal, **25**, (1903)
[4] *Ztschr. phys. Chem.*, **42**, 637.
[5] *Ztschr. anorg. Chem.*, **35**, 45.
[6] *Chem. Ztg.*, **27**, 918.
[7] *Ber. d. chem. Ges.*, **36**, 3759.
[8] *Ibid.*, **36**, 4299.

refuse in the way of stems and leaves was removed before cooking.

DETAILS AS TO COOKING.

Broccoli.—This vegetable was well soaked in cold water, then removed and placed in an uncovered sauce-pan containing boiling water, being briskly boiled for about fifteen minutes, then removed and allowed to drain on a sieve. No salt or sugar was added during the process.

Brussels Sprouts.—When ready for cooking, the sprouts were put into plenty of boiling water, and treated in the same way as the broccoli. No pepper or salt was added.

Asparagus.—The ordinary small variety was used, the sticks being first washed and scraped, then tied into bundles of twelve and the white ends cut even. The bundles were placed in an open sauce-pan containing hot water, which was not allowed to cover the heads; the boiling was continued for fifteen minutes, the bundles were then removed from the pan and the excess of water drained off on a sieve. No salt or vinegar was used in the cooking, and the hard portion of stems was removed before the estimation of water.

Green Artichokes.—These were placed in boiling water in an uncovered sauce-pan, and boiled for two hours. No salt or potash was added to the water. When cooked, the heads were allowed to drain on a sieve; all the leaves and fibrous portions were removed and only the fleshy receptacle of the flowers was analyzed.

Leeks.—This vegetable was cooked in a similar way to the green artichokes, in boiling water, without the addition of salt.

Oatmeal.—The variety used was coarse Scotch; two tablespoonfuls were gently added to a pint of boiling water, well stirred all the time, then gently boiled for half an hour and stirred now and again ; no salt was added. In the case of the milk porridge, two tablespoonfuls of the oatmeal were well stirred in a little cold water, the mixture was allowed to clear and the water poured off; ½ pint of milk and ½ pint of water were added to the oatmeal and the whole briskly boiled for half an hour.

Dried Peas.—They were first soaked for several hours in cold water, then tied in a cloth and put into a sauce-pan containing cold water, but no salt or sugar; they were allowed to simmer

for three hours until tender, when they were ready to be drained on a colander.

Tapioca (Flake).—Two ounces were first soaked in a pint of water for twenty minutes, then put on the fire in a stew-pan; the mixture was well stirred until it boiled; the pan was then drawn to the side of the fire and allowed to simmer until the tapioca was soft.

Lentils.—The red variety was used. The lentils were well soaked for about three hours in cold water, when they were put into a sauce-pan with plenty of cold water and briskly boiled for half an hour, then allowed to simmer until soft, when they were drained on a colander.

Rice.—The sample used was Carolina. The rice was first washed and then placed on a sieve to drain, when it was ready to be shaken into boiling water; it was then briskly boiled, while occasionally stirred, until it was quite tender, and ready to be drained on a colander.

Macaroni.—Prepared in Genoa. The first process was to break the sticks up into short lengths, ready to be plunged into boiling water; the boiling was kept up for about half an hour, when the process was arrested by adding cold water, and the macaroni was drained over a colander. No salt was used in the cooking.

Rhubarb.—The pink variety was the one used. The leaf stems were cut into short lengths, and the stewing was done without the addition of sugar.

Baked Beans.—The variety used was the Thubber Brand, New York.

Petit Pois.—The tin was marked "Victor Fertrais, a bel abord sur Sevre, Nantes." The contents of the tin were drained on a sieve; the filtrate consisted of 269 cc. liquid, which, on evaporation, left 11.54 grams of solid, 3.65 grams of which were protein.

All these vegetable foods were boiled in undistilled water, as supplied by the Bristol Water Company, which shows about 26° of hardness, chiefly due to calcium carbonate.

Every sample was weighed before and after cooking, as is shown in Table I; also the percentages of refuse in the raw and cooked conditions are given, as well as the percentage of edible matter, and the price per pound of the raw material.

TABLE I.

	Price per pound in pence.	As purchased. Refuse—green leaves and stems. Per cent.	As purchased. Used for cooking. Per cent.	As served at table. Refuse—leaves and stems. Per cent.	As served at table. Edible portion. Per cent.	Weight before cooking. Grams.	Weight after cooking. Grams.
Brussels sprouts	2½	6.34	93.66	....	100.00	100	121.0
Rice	4	....	100.00	....	100.00	100	418.0
Rhubarb	2¼	19.55	80.45	....	100.00	...	....
Lentils	2½	....	100.00	....	100.00	100	238.4
Oatmeal (water)	2½	....	100.00	....	100.00	100	280.3
Oatmeal (milk)	..	....	100.00	....	100.00	100	254.6
Asparagus	9½	35.13	64.87	34.18	65.82	100	56.9
Peas	2½	....	100.00	....	100.00	100	210.1
Tapioca	5	....	100.00	....	100.00	100	430.3
Artichokes	2½	72.70	27.30	68.71	31.29	100	336.1
Petit pois	5¼	....	100.00	....	100.00	...	....
Baked beans	5¼	....	100.00	....	100.00	...	....
Leeks	1½	74.69	25.31	....	100.00	100	187.5
Macaroni	8	....	100.00	....	100.00	100	252.4
Broccoli	1¾	67.97	32.03	....	100.00	100	99.5

ANALYSIS OF THE EDIBLE PORTION.

Determination of Water.—Every sample of the green, cooked vegetables, and also of the cooked cereals, was broken up into small pieces, the surface water being removed before the process of drying was commenced. A small portion, from 20-50 grams of the vegetable substance, was weighed in an evaporating dish, and heated from twelve to twenty-four hours, first in a steam-bath and then in an air-bath at a temperature not exceeding 110°. When the sample was fairly firm it was allowed to cool in a desiccator, weighed again, and reduced to powder in a coffee-mill. A portion of the powder was again weighed, placed in the air-bath and kept at a temperature not exceeding 110° until the weight remained constant; from these results the percentage of water was calculated. Two estimations were made in every case.

Fat.—The fat and coloring-matters, when present, were extracted from the powdered foods by ether. From 4 to 6 grams were placed in a wide glass tube, the narrower and lower end of which was closed with a plug of cotton wool, and passed through a cork into a small flask of about 100 cc. capacity, con-

taining ether; the upper end of the tube was connected with a reflex Liebig condenser. The flask was heated by a water-bath; the ethereal vapors passing through the cotton wool to the powdered substance were condensed in the condenser, and the ether dissolved the oil as it passed back through the tube into the cooled flask; the process was repeated until a drop on evaporation left no residue; when all the soluble matter had been extracted, the ether was distilled off and the residue weighed.

Woody Fiber.—The method used in this portion of the work was that described by Dr. H. W. Wiley in "Principles and Practice of Agricultural Chemistry," Vol. III, p. 303. About 2 grams of the residue from the determination of fat was used in each case, and was boiled first with 200 cc. of 1.25 per cent. sulphuric acid; after filtration, the residue was washed with boiling water until the washings were no longer acid. It was then boiled with 200 cc. of 1.125 per cent. solution of sodium hydroxide, nearly free from sodium carbonate, next filtered into a Gooch crucible, washed with boiling water, then dried at 110°, weighed and incinerated completely, the loss of weight giving the percentage of fiber.

Ash.—Some of these determinations were made by burning a weighed portion of the substance in a platinum boat inside a glass tube, through which a current of oxygen was passing; it was, however, found that satisfactory results could be obtained by incinerating in a platinum crucible; exhaustion with water was not required.

Cellulose.—This determination was made by means of the potassium chlorate method originally suggested by F. Schulze.[1] From 2 to 6 grams of the powdered substance were digested with 12 parts of nitric acid (sp. gr. 1.10) and 0.8 part of potassium chlorate in a closed flask, and kept for about a fortnight at a temperature below 15°. Distilled water was then added and the liquid siphoned off; the residue was washed into a beaker with dilute ammonia (1 part strong ammonia to 50 of water) and heated for about forty-five minutes at 60°; next the residue was thrown on a weighed filter and washed with the dilute ammonia till the filtrate was colorless; it was then washed successively with cold and with hot water, alcohol and ether; it was finally

[1] *Chem. Centrbl.*, 1857, p. 321.

dried and weighed. Any nitrogenous matter present was estimated by Kjeldahl's method, and ash by ignition.

Nitrogen.—Kjeldahl's method, modified to include the nitrogen of nitrates, as given in Bulletin 46, U. S. Department of Agriculture, Division of Chemistry, was used in the determination of nitrogen. At least three estimations were made.

Protein.—The protein was calculated by multiplying by 6.25 the nitrogen, as before determined by Kjeldahl's method.

Starch or Carbohydrates by Direct Inversion with Hydrochloric Acid.—The starch was indirectly determined by inversion into glucose. In former investigations with vegetables[1] the usual method given in text-books was employed, but, on titrating with Fehling's solution, in the case of green vegetables, a blue or white precipitate came down. A modification of the method was tried and proved successful, and was therefore employed in this set of investigations. Solutions were prepared as suggested by Sachsse.[2] A weighed portion of the vegetable powders was digested with 10 cc. of hydrochloric acid (sp. gr. 1.125) and 100 cc. of water, in a flask connected with a reflex condenser; the whole was briskly boiled for three hours, and the solution filtered. Instead of neutralizing with sodium hydroxide, the filtrate was treated with basic acetate of lead, and a current of sulphur dioxide was passed through the liquid to precipitate any excess of lead present. The solution was filtered and washed, and alumina was added until no more was dissolved; it was concentrated at 100° and, when necessary, boiled with animal charcoal and a few drops of milk of lime, and finally filtered before titrating with Fehling's solution; the latter was prepared according to the usual method, and standardized by the directions given by Roscoe and Schorlemmer in the "Treatise on Chemistry."[3] Each cubic centimeter of Fehling's solution was calculated as equivalent to 0.05 gram of anhydrous glucose, or 0.045 gram of starch.

Sulphur and Phosphorus.—These estimations were made by fusion with mixtures of sodium carbonate and potassium nitrate; the sulphur was determined as barium sulphate, and the phosphorus precipitated as magnesium ammonium phosphate, which was dissolved in a solution of acetic acid, reprecipitated,

[1] *Trans. Chem. Soc.* (London), 1892, p. 236.
[2] *Chem. Centrbl.*, 8, 639 and 732.
[3] Vol. III, Part 2, p. 519.

and ignited; the percentage was calculated from the pyrophosphate after ignition.

As stated in the beginning of this paper, the work described was undertaken with the idea of arriving at a clearer knowledge of the composition of vegetable foods as served at table. It is difficult to compare the results obtained with those of other investigators, for even in the raw condition great differences in composition occur, and the differences are necessarily greater after cooking. It may be noticed that almost all the vegetable substances become more watery in the process of cooking, the exceptions being broccoli, where the weight of the raw and cooked conditions is practically the same, while in the case of asparagus a considerable decrease of weight takes place in the process of cooking, due probably to the loss of soluble nitrogenous compounds; this latter article of food is rendered expensive by its large percentage of waste, both before and after cooking. With regard to the green artichokes, it may be pointed out that in the raw condition this is a somewhat tough vegetable, and in the process of cooking absorbs a larger proportion of water than the other green vegetables. It will be observed from the details given that the liquor in which all the foods were cooked, except in the case of oatmeal and tapioca, was poured off, and thus, as shown in Bulletin 43, U. S. Department of Agriculture, all matter in solution is lost; "as ordinarily cooked, carrots lose one-quarter of their nutritive value." "In 100 pounds of uncooked cabbage there are but 7½ pounds of dry matter, and of this dry matter 2¼ to 3 pounds are lost in the process of cooking."

Table II gives full details of the analysis of the dried, powdered vegetable foods, showing the percentages of ash, protein (calculated from nitrogen), woody fiber, fats, and cellulose, the starch by difference, also by inversion, a column headed undetermined being added to bring the total results up to 100 in the latter case. Ultimate analyses are also given for the nitrogen, phosphorus and sulphur.

Table III gives the proximate analyses calculated on the materials in their natural moist condition, in order to more clearly show the true nutritive value of the foods under consideration.

TABLE II.—COMPOSITION OF THE EDIBLE PORTION OF THE COOKED VEGETABLE FOODS.

	Proximate analysis of the water-free substance.							Ultimate analysis of the dried substance.		
	Ash.	Protein (N × 6.25).	Fat (ether extract).	Woody fiber.	Cellulose.	Starch.	Undetermined.	Ash, protein, fats, woody fiber, and cellulose.	Starch by difference.	Nitrogen.	Sulphur.	Phosphorus.
Broccoli	6.93	30.18	2.94	12.17	11.49	31.67	4.52	63.71	36.29	4.83	1.53	0.79
Brussels sprouts	5.22	26.50	2.09	10.51	9.88	40.03	4.70	55.27	44.73	4.23	0.40	0.21
Rice	0.31	6.83	0.08	0 13	0.46	82.42	9.78	7.80	92.20	1.26	0.23	0.10
Rhubarb	11.97	12.87	1.87	15.93	16.44	36.02	4.00	49.08	40.92	2.06	0.69	0.64
Macaroni	0.70	15.62	0.34	0.68	0.43	82.58	....	17.72	82.28	2.50	0.18	0.23
Lentils	2.07	26.00	0.57	1.34	2.43	60.48	7.11	32.41	67.59	4.16	0.29	0.91
Asparagus	10.15	29.99	1.34	9.24	16.96	30.27	1.85	67.88	32.12	4.80	1.27	1.30
Leeks	5.82	10.46	0.97	11.08	11.07	56.21	4.36	39.40	60.60	1.68	1.18	0.98
Oatmeal (water)	4.25	13.62	5.86	2.15	0.49	67.34	6.29	26.37	73.63	2.13	0.34	0.17
Oatmeal (milk)	4.34	12.31	5.89	1.13	2.35	73.16	0.62	26.02	73.98	1.96	0.81	1.12
Peas	1.79	24.87	1.87	5.98	6.71	61.27	....	41.32	58.68	3.93	0.29	0.95
Tapioca	0.50	3.00	0.17	0.18	0.22	85.91	10.02	4.07	95.93	0.48	0.55	0.20
Green artichokes	7.54	19.31	1.76	6.66	11.15	50.51	3.07	46.42	53.58	3.09	1.44	0.57
Petit pois	4.00	27.06	0.44	13.21	9.01	56.46	....	53.72	46.28	4.33	0.22	0.22
Baked beans	5.56	15.53	0.59	3.74	0.64	67.32	9.65	23.06	76.94	2.48	0.18	0.06

TABLE III.—PROXIMATE ANALYSIS CALCULATED FOR THE MATERIALS IN THEIR NATURAL MOIST CONDITION.

	Water.	Ash.	Protein (N × 6.25).	Woody fiber.	Cellulose.	Fats.	Starch.	Undetermined.	Ash, protein, fats, woody fiber, water, cellulose.	Starch by difference.
Broccoli	91.69	0.58	2.53	1.02	0.96	0.24	2.63	0.60	96.77	3.23
Brussels sprouts	89.27	0.56	2.84	1.12	1.05	0.07	4.29	0.80	94.91	5.09
Rice	80.93	0.06	0.13	0.02	0.09	0.01	16.87	0.89	82.24	17.76
Rhubarb	95.25	0.56	0.61	0.75	0.77	0.09	1.74	0.23	98.03	1.97
Macaroni	66.13	0.23	5.59	0.23	0.14	0.11	27.90	...	72.43	27.57
Lentils	66.04	0.70	8.82	0.45	0.82	0.19	20.53	2.45	77.02	22.98
Asparagus	93.04	0.70	2.08	0.64	1.18	0.09	2.10	0.17	97.73	2.27
Leeks	86.12	0.80	1.45	1.53	1.52	0.13	7.80	0.65	91.55	8.45
Oatmeal (water)	72.54	1.16	3.74	0.59	0.13	1.84	18.48	1.72	79.80	20.20
Oatmeal (milk)	64.74	1.55	4.39	0.40	0.84	2.10	25.96	0.02	74.02	25.98
Peas	62.18	0.67	9.40	2.21	2.53	0.70	23.16	...	77.69	22.31
Tapioca	80.62	0.09	0.58	0.03	0.04	0.03	16.65	3.55	79.80	20.20
Green artichokes	84.72	1.15	2.95	1.01	1.70	0.26	7.68	0.53	91.79	8.21
Petit pois	84.18	0.63	4.28	2.13	1.42	0.06	8.92	...	92.70	7.30
Baked beans	69.85	1.78	4.99	1.20	0.20	0.19	21.69	2.10	76.21	23.79

Clifton, Bristol, England.

INVESTIGATION OF THE BODIES CALLED FIBER AND CARBOHYDRATES IN FEEDING-STUFFS, WITH A TENTATIVE DETERMINATION OF THE COMPONENTS OF EACH.[1]

BY P. SCHWEITZER.

Received December 30, 1903.

THE results of a continuation and extension of the work of which a preliminary part was published in the Annual Report of the Missouri Agr. Expt. Station for 1898 are here presented. Ten substances—two of corn stalks, two of corn leaves, three of timothy hay, two of red clover, and one of blue grass—were selected for the purpose. The character and composition of these, as ascertained by the Official Agricultural Chemists' method, all determinations being in duplicate and made with great care under conditions as nearly alike for the same groups of bodies

[1] Read at the St. Louis meeting of the American Chemical Society. The larger part of the laboratory work was done by Mr. W. B. Cady.

in the different feeds as it was possible to maintain, are tabulated in Table I. The carbohydrates are, of course, given by difference and, for comparison's sake, the percentages also of the fibers by the chlorate and bromine methods. Both of these methods, described by Dr. Hugo Müller under Pflanzenfaser on pages 26 and 27 of the "Bericht über die Entwickelung der chemischen Industrie, 1877, by Dr. A. W. Hofmann," were modified, as necessity seemed to require, yet without, it is believed, seriously interfering with the quantitative production of a fairly pure fiber.

The percentages of fiber by the three methods are, as was expected, different and may be compared in Table II, which is calculated for water and ash-free material. The differences in the fibers affect, of course, also the carbohydrates and, while the official and chlorate methods yield results that, by averaging, come near one another, those by the bromine method are much higher for fiber and correspondingly lower for carbohydrates, through retaining the pectose bodies, shown in the published preliminary investigation to be present.

The percentages of ash in the fibers are quite large and are given, along with the nitrogen, as averages for each ten samples at the bottom of the table.

The Ultimate Composition of the fibers[1] obtained by the three methods is given in Table III, calculated for ash, nitrogen and water-free material; that of the portions dissolved by the Schweizer reagent and precipitated by hydrochloric acid is added for the sake of comparison. It will be seen that in no instance do we deal with chemically pure cellulose; the oxygen falls in twenty-nine of the thirty analyses below the requirements of the hydrogen to form water and it would, therefore, be plainly useless to construct any symbols for the fibers analyzed. The bodies recovered from their solution in the ammoniacal copper solution, likewise, differ slightly from one another, yet, on the whole, they are what G. Bumcke and R. Wolfenstein[2] call the lactone of the acid cellulose, the percentage composition of which is closely approached by the average of the three analyses given.

[1] The requisite quantity of fiber by each of the three methods was prepared by treating successively 2 grams of the material until about 6 grams of crude fiber was obtained. This, finely ground, furnished the material for this and the other work of the investigation.

[2] *Ber. d. chem. Ges.*, **32**, 4293.

If symbols for these compounds were to be offered, they might be as follows:

$C_{44}H_{70}O_{37}$ by O. A. C. method $C_{43}H_{75}O_{38}$ by chlorate method $C_{43}H_{74}O_{37}$ by bromine method	*Percentage Composition:* C = 43.64 H = 6.34 O = 50.02
$C_{36}H_{60}O_{31}$ B. & W.'s lactone.	C = 43.73 H = 6.07 O = 50.20

The Calorific Values of the different fibers, ascertained by the bomb-calorimeter with completely dried material, may be averaged for each of the three methods and compared with that for pure cellulose. The official method produces a product richer in carbon than the others caused, probably through retaining a greater quantity of encrusting material; the values, in calories per gram, are:

Fiber by O. A. C. method (average)	4408.
Fiber by chlorate method (average)	4249.
Fiber by bromine method (average)	4170.
Cellulose	4200.

Treatment of the Crude Fiber with the Schweizer Reagent.— The reagent itself was prepared in the following manner: 300 grams of chemically pure copper sulphate were dissolved in 6 liters of water, 30 grams of ammonium chloride added and the copper hydroxide precipitated by cautious additions of a dilute solution of sodium hydroxide to slight excess. The precipitate was then washed free from alkali by decantation and dissolved by strong ammonia so as to yield a fluid containing about 15 per cent. of the latter.

One-half gram of the water-free fiber was then digested for twenty-four hours in a closed flask of 200 cc. capacity with 100 cc. of the reagent with frequent shaking. Water was then added and the solution filtered through asbestos by means of the suction-pump and, after sufficient washing, the residue dried to constant weight at from 100° to 105° C. The filtrate, in turn, was acidulated with hydrochloric acid and set aside for twenty-four hours, when the liquid was carefully decanted off, and the precipitate finally washed on the filter and dried and weighed. The operations described were in all cases slow and difficult, especially so with the materials from Nos. 1411 and 1425, as the undissolved residues, as well as the re-precipitated cellulose materials, were all more or less gelatinized and required special precautions for

successful washing. The direct weighing of the two bodies, however, permitted now the estimation, by difference, of the amount of the fiber dissolved by this reagent, as well as the amount kept in solution after acidulation. All operations were conducted as nearly alike in manner, time and strength of solution used, as was possible, and the results may be taken as fairly accurate and comparable.

It is seen from Table IV that the action of the O. A. C. method on the fibers is not as powerful as that of the chlorine and bromine methods; for the average percentage of the fibers undissolved by the former is 14.07, while amounting to only 2.29 and 3.28 in the cases of the others. Corresponding to these effects, we find the hydrolyzed or inverted portions of the materials by the three methods to be 10.32, 14.14 and 24.96 per cent. of the original amounts operated upon.

Furfural Obtained from Feeds and Fibers.—Two grams of finely ground dry substance were brought into an Erlenmeyer flask of 300 cc. capacity, connected with a Liebig condenser and separatory funnel by a 2-hole rubber stopper, and 100 cc. of hydrochloric acid of specific gravity 1.06 were added. The flask was then heated on wire gauze so that about 30 cc. distilled over every fifteen minutes; with every such portion having passed over, 30 cc. of the acid were added so as to enter the flask at about the same rate as the distillate left it, keeping the contents of the flask throughout as near 70 cc. as possible. The flask was shaken from time to time to bring down the particles that would adhere to its sides.

The distillation was continued until a drop of the distillate on a slip of filtering paper, moistened with aniline acetate, gave no red coloration, yielding in the cases here described from 250 cc. to 350 cc. of furfural-containing liquid. The distillate was then neutralized with sodium carbonate, made slightly acid with acetic acid and brought up to 500 cc. with a salt solution of 208 grams of salt to the liter, and 10 cc. of phenyl hydrazine acetate added (10 grams of phenyl hydrazine, 7.5 grams of glacial acetic acid to 100 cc. of solution). The whole was then stirred for one-half hour with a rubber-tipped stirring rod when the hydrazone began to separate out in fine orange-red crystals; set aside for twenty-four hours, the precipitate was now collected in a Gooch

crucible on asbestos by aid of the suction-pump and washed with 100 cc. of water; the precipitate being slightly soluble, the same amount of wash-water was used in every instance. The hydrazone could be removed without difficulty from the sides of the beaker by means of the stirring rod, except in a few cases where it seemed to be gummy and had to be dissolved by alcohol; in these the alcoholic liquid was evaporated and the slight residue weighed separately. The suction-pump was run five minutes after washing the main precipitate so as to remove most of the water, when it was placed for three hours in a vacuum oven heated to 65° to 70°, while a current of dry air passed slowly over it. At the expiration of this time, crucible and contents were cooled and weighed, the contents dissolved with warm alcohol, the crucible dried and weighed again and the difference in weight taken as furfural hydrazone, from which, by multiplication with 0.538, the furfural itself was derived. The method, as tested with known weights of furfuramid, especially prepared for this purpose, gave sufficiently reliable and accurate results and was, on the whole, not excessively troublesome.[1]

From the values thus obtained the percentages, and weights in grams from so much of the fibers as are contained in 100 grams of the feeds, are found and from these again percentages and quantities of pentosan in the feeds are derived by multiplication with 1.84 and given in Table V.

The Determination of Sugar and Starch in the nine samples of feed (the material of No. 1426 had unfortunately given out) was made by washing out the sugar with cold water and inverting it, as also the residue, by the usual O. A. C. method and making the calculations from the weights of the reduced copper. The correction for starch was made by subtracting from the reduced copper, as found, the quantity of it reduced by the pentosan, *i. e.*, the pentosan which was readily invertible, not the portion remaining with the fiber and subsequently determined by treatment with stronger acid. The values are given in Table VI.

[1] The furfuramid, after recrystallization, was drained, pressed between filtering paper and carefully air-dried. One gram of it should yield 1.0746 grams of furfural. Experiment yielded in two trials, taking in each case 0.3 gram (0.3224 gram of furfural), 0.3012 gram and 0.2959 gram. A third and fourth determination, made with 2 grams of feed (No. 1416), to which had been added 2 grams of furfuramid (0.2149 gram furfural), yielded respectively 0.4140 gram and 0.4455 gram furfural or, subtracting that from the feed itself 0.1822 gram and 0.2137 gram. Considering the difficulty of obtaining perfectly dry and undecomposed furfuramid, the results are acceptable.

The Conclusions of the Investigation are tabulated in Table VII and will be readily understood. The contents of the feeds by the O. A. C. method in fiber and carbohydrates, the latter, of course, by difference, are placed at the head and, below, follow the true values for fiber with such individual carbohydrate components as could be determined by a combination of methods. The true value for fiber is the crude fiber less the furfural-yielding complex retained by it, calculated as pentosan. In this, then, a differentiation in the two groups of bodies occurring in crude fiber has been made, resulting in a more correct value for fiber as well as for carbohydrates. In the table, this pentosan is given separately as fibro-pentosan to indicate its origin.

As pectoses, are counted the substances remaining with the fiber by the bromine method and removable by treatment with acid and alkali, as shown in the paper published in the annual report previously referred to. The fiber values by the O. A. C. method subtracted from those of the bromine method furnished, consequently, the values of pectose which, on comparison, agree fairly well with those from similar material in 1898. These pectoses are now found to yield furfural as well as the fibers, for on subtracting one fiber from the other we subtract also, of course, the pentosan retained by it and, as the latter fiber yields a much larger amount of this than the former, the difference must be attributed to the pectose complex; it is indicated in the table as pecto-pentosan and made to serve, by difference again, to yield the pentosan derived, in part from sugar and starch, but in the main from the carbohydrates of unknown composition and character present.

A comparison of these three values is not without interest, averaging for the ten feeds as follows:

13.43 per cent. of pentosan from fiber;
26.23 per cent. of pentosan from pectose;
54.73 per cent. of pentosan from indefinite carbohydrates.

The need of additional investigation in certain definite directions is seen plainly.

TABLE I.—PERCENTAGE COMPOSITION OF FEEDS (O. A. C. METHOD) CALCULATED FOR WATER-FREE MATERIAL.

Mark.	No.	Water.	Albuminoid nitrogen.	Amido nitrogen.	Protein.	Ether extract.	Crude fiber. O. A. C. method.	Crude fiber. Chlorate method.	Crude fiber. Bromine method.	Carbohydrates.	Ash.
Corn stalks, just before blooming.....	1427	9.14	0.858	0.547	8.810	2.730	26.36	30.61	40.24	55.79	6.31
Corn stalks, seed in dough	1464	5.62	0.445	0.016	2.880	1.710	34.20	36.10	44.61	54.73	6.48
Corn blades, just before blooming	1426	7.82	2.690	0.500	19.940	4.570	20.57	24.05	35.33	45.50	9.42
Corn blades, seed in dough.....	1465	7.63	1.450	0.110	9.750	3.550	21.04	24.42	33.72	53.27	12.39
Timothy, just heading.....	1412	7.85	0.928	0.532	9.120	2.520	32.44	32.65	48.99	49.58	6.34
Timothy, coming into bloom.....	1416	7.95	1.130	0.080	7.560	3.280	34.66	35.82	47.03	46.62	7.88
Timothy, seed ripe	1463	7.59	0.666	0.016	4.260	2.220	36.31	33.48	43.00	52.55	4.66
Red clover, in bloom	1411	8.03	2.110	0.800	18.130	5.360	23.38	23.23	28.17	45.39	7.74
Red clover, seed ripe	1425	8.95	1.780	0.170	12.310	4.050	30.00	26.62	39.10	46.95	6.69
Blue grass, seed ripe	1413	7.54	1.090	0.110	7.500	2.950	33.99	32.73	46.74	47.97	7.59

TABLE II.—PERCENTAGES OF CRUDE FIBER AND CARBOHYDRATES, CALCULATED FOR ASH AND WATER-FREE MATERIAL.

	O. A. C. method.		Chlorate method.		Bromine method.	
No.	Fiber.	Carbohydrates.	Fiber.	Carbohydrates.	Fiber.	Carbohydrates.
1427	28.14	59.55	32.67	55.01	42.95	44.73
1464	36.57	58.52	38.60	56.49	47.70	47.39
1426	22.71	50.23	26.55	46.39	39.00	33.94
1465	24.02	60.80	27.87	56.94	38.49	46.33
1412	34.64	52.94	34.86	52.71	52.31	35.26
1416	37.62	50.61	38.88	49.35	51.05	37.18
1463	38.08	55.12	35.12	58.09	45.10	48.10
1411	25.34	49.20	25.18	49.36	30.53	44.01
1425	32.15	50.32	28.53	53.94	41.90	40.56
1413	36.78	51.91	35.42	55.44	50.58	40.28
	Average per cent. of ash and nitrogen in fibers.					
	0.705		1.328		0.839	

TABLE III.—ULTIMATE COMPOSITION OF THE CRUDE FIBERS BY THE THREE METHODS, CALCULATED FOR ASH, NITROGEN, AND WATER-FREE MATERIAL.

	O. A. C. method.			Chlorate method.			Bromine method.		
No.	Carbon.	Hydrogen.	Oxygen.	Carbon.	Hydrogen.	Oxygen.	Carbon.	Hydrogen.	Oxygen.
1427	44.35	6.50	49.15	44.95	6.32	48.73	44.43	6.40	49.17
1464	44.73	6.25	49.02	44.81	6.38	48.81	44.03	6.18	49.79
1426	44.48	6.39	49.13	42.90	6.31	50.79	44.55	6.62	48.83
1465	46.17	6.74	47.09	45.12	6.39	48.49	44.79	6.57	48.64
1412	44.22	6.57	49.21	44.72	6.38	48.90	44.14	6.22	49.64
1416	44.47	6.48	49.05	44.98	6.54	48.48	44.49	6.41	49.10
1463	44.98	6.39	48.63	44.83	6.43	48.74	44.06	6.48	49.46
1411	46.55	6.42	47.03	44.43	6.39	49.18	44.61	6.50	48.89
1425	47.06	6.54	46.40	45.05	6.45	48 50	44.99	6.48	48.53
1413	44.72	6.40	48.88	44.89	6.47	48.64	44.50	6.73	48.77
	Composition of that part of the fiber dissolved by and reprecipitated from the Schweizer reagent.								
	44.06	6.59	49.35	43.00	6.28	50.72	43.85	6.15	50.00

TABLE IV.—TREATMENT OF THE CRUDE FIBERS WITH AMMONIACAL COPPER SOLUTION. PERCENTAGES OF UNDISSOLVED FIBER AND OF CELLULOSE RECOVERED BY PRECIPITATION; ALSO, BY DIFFERENCE, THE PERCENTAGES OF DISSOLVED AND HYDROLYZED SUBSTANCE.

	O. A. C. method.				Chlorate method.				Bromine method.			
No.	Undissolved.	Dissolved.	Reprecipitated.	Hydrolyzed.	Undissolved.	Dissolved.	Reprecipitated.	Hydrolyzed.	Undissolved.	Dissolved.	Reprecipitated.	Hydrolyzed.
1427	1.00	99.00	92.38	6.62	0.00	100.00	80.00	20.00	0.10	99.90	74.80	25.10
1464	5.62	94.38	78.18	16.20	1.60	98.40	88.80	9.60	1.09	98.91	78.40	20.51
1426	4.82	95.18	89.40	5.78	2.80	97.20	82.50	14.70	1.64	98.36	71.48	26.88
1465	3.90	96.10	80.00	16.10	1.92	98.08	87.00	11.08	3.40	96.60	67.27	29.33
1412	5.40	94.60	82.40	12.20	3.20	96.80	79.04	17.76	3.42	96.58	68.80	27.78
1416	12.50	87.50	78.80	8.70	3.56	96.44	86.00	10.44	5.62	94.38	71.40	22.98
1463	26.48	73.52	62.50	11.02	0.40	99.60	88.00	11.60	3.40	96.60	69.00	27.60
1411	34.58	65.42	57.20	8.22	3.20	96.80	80.00	16.80	4.60	95.40	74.10	21.30
1425	34.48	65.52	58.00	7.52	3.40	96.60	81.48	15.12	6.30	93.70	68.40	25.30
1413	11.90	88.10	77.20	10.90	2.80	97.20	82.90	14.30	3.20	96.80	74.00	22.80

TABLE V.—PER CENT. OF PENTOSANS IN DRY AND ASH-FREE MATERIAL, CALCULATED FROM FURFURAL; FACTOR 1.84.

	Per cent. of pentosan in feed and fiber.				Grams of pentosan in fiber from 100 grams of feed.		
		Fibers by					
No.	Feed.	O. A. C. method.	Chlorate method.	Bromine method.	O. A. C. method.	Chlorate method.	Bromine method.
1427	23.13	16.93	13.91	25.74	3.74	4.52	11.00
1464	27.25	14.94	16.80	24.14	5.43	6.41	11.47
1426	23.39	16.85	17.26	29.02	3.79	4.41	11.23
1465	25.10	15.11	19.45	30.54	3.53	5.20	11.27
1412	17.46	13.21	19.34	24.49	4.56	6.65	12.74
1416	23.15	13.01	16.71	23.64	4.87	6.41	12.01
1463	25.23	15.33	15.84	27.51	5.79	5.51	12.34
1411	14.06	11.94	9.81	16.87	3.00	2.44	5.11
1425	16.65	12.84	11.42	21.67	4.11	3.23	8.96
1413	23.90	13.28	19.83	26.64	4.86	6.93	13.38
Average,	21.93	14.04	16.04	25.03	4.37	5.17	10.95

TABLE VI.—PER CENT. OF SUGAR AND STARCH IN WATER AND ASH-FREE FEEDS.

Per cent. of		Starch and pentosans calculated as starch.
Sugar.	Starch.	
20.69	...	19.39
2.31	1.42	23.56
...	...	....
3.20	2.02	23.89
2.91	9.24	21.99
3.16	6.12	24.96
3.82	6.19	26.29
3.86	12.01	23.56
4.58	4.84	17.46
3.45	6.34	24.39

UNIVERSITY OF MISSOURI, COLUMBIA, MO.

TABLE VII.—PER CENT. OF CRUDE FIBER AND CARBOHYDRATES IN THE WATER AND ASH-FREE FEEDS BY O. A. C. METHOD, AND OF SPECIAL CONSTITUENTS BY THE COMBINATION OF METHODS PURSUED IN THIS INVESTIGATION.

Number of sample	1427	1464	1426	1465	1412	1416	1463	1411	1425	1413
Crude fiber	28.14	36.57	22.71	24.02	34.64	37.62	38.08	25.34	32.15	36.78
Carbohydrates	59.55	58.52	50.23	60.80	52.94	50.61	55.12	49.20	50.32	51.91
Total,	87.69	95.09	72.94	84.82	87.58	88.23	93.20	74.54	82.47	88.69
Pure fiber	24.40	31.14	18.92	20.49	30.08	32.75	32.29	22.34	28.04	31.92
Fibro-pentosan	3.74	5.43	3.79	3.53	4.56	4.87	5.79	3.00	4.11	4.86
Pectose	7.55	5.09	8.85	6.73	9.49	6.29	0.47	3.08	4.90	5.28
Pecto-pentosan	7.26	6.04	7.44	7.74	8.18	7.14	6.55	2.11	4.85	8.52
Pentosan	12.13	15.78	12.16	13.83	4.72	11.14	12.89	8.95	7.65	10.52
Sugar	20.69	2.31		3.20	2.91	3.16	3.82	3.86	4.58	3.45
Starch	....	1.42	21.78	2.02	9.24	6.12	6.19	12.01	4.84	6.34
Indefinite carbohydrates	11.92	27.88		27.28	18.40	16.76	25.20	19.19	23.50	17.80
Total,	87.69	95.09	72.94	84.82	87.58	88.23	93.20	74.54	82.47	88.69

THE DETERMINATION OF GLIADIN IN WHEAT FLOUR BY MEANS OF THE POLARISCOPE.[1]

By Harry Snyder.

Received January 9, 1904.

Wheat proteids have been studied by a number of investigators. Ritthausen,[2] one of the earliest workers, recognized four wheat proteids: (1) Gliadin, soluble in warm dilute alcohol from which it is precipitated on cooling; (2) mucedin, similar to gliadin, but less soluble in strong alcohol; (3) gluten-casein, insoluble in alcohol, but soluble in a dilute alkali solution; and (4) glutin-fibrin. Osborne and Voorhees[3] have separated five proteids from wheat: (1) An albumin (leucosin) soluble in water; (2) a proteose body; (3) a globulin (edestin) soluble in a dilute salt solution; (4) and (5) two insoluble proteids, gliadin and glutenin. Gliadin is soluble in a dilute alcohol solution and glutenin in a dilute alkali solution.

From 85 to 90 per cent. of the total proteids of wheat flour are in the form of gliadin and glutenin. In most flours gliadin predominates and constitutes from 55 to 70 per cent. of the total proteid matter. The total protein in wheat flour can be accurately determined by the factor $N \times 5.70$, in which N represents the per cent. of total nitrogen as determined by the Kjeldahl process. The amount of non-proteid nitrogen in sound wheat flour is so small that for practical purposes it can be disregarded.

The gliadin can be determined by extracting a weighed amount of flour with dilute alcohol. I have found the following method, based largely upon the work of Osborne and Voorhees, to give satisfactory results.[4] Five grams of flour are weighed into a flask and 250 cc. of 70 per cent. alcohol added; the flask is shaken at half-hour intervals for three hours. After twelve to eighteen hours the alcohol is filtered off, and to 100 cc. of the filtrate in a Kjeldahl digestion flask are added about 3 cc. of sulphuric acid. The flask is placed in a water-bath and the alcohol evaporated.

[1] Read at the St. Louis meeting of the American Chemical Society.

[2] "Die Eiweisskorper der Getreidearten, Hulsenfruchte und Oelsamen." Bonn, 1872. (Contains references to his earlier publications.)

[3] *Am. Chem. J.*, **15**, 392 (1893).

[4] "Proteids of Wheat Flour," Minnesota Expt. Sta. Bull. No. 63, p. 520.

The remainder of the acid is then added and the determination of the nitrogen completed in the usual way.

While this method gives accurate results, it is not applicable to the technical work of flour testing because too much labor, expense, and time are involved in the various operations. Since the proteids have well-defined optical properties, equally as much as have the sugars, methods based upon the use of the polariscope appear to offer a possible solution to the problem of determining the gliadin content of wheat flour without sacrificing accuracy, and at the same time securing a more rapid and inexpensive method.

The determination of the specific rotary power of gliadin, as reported by Kjeldahl,[1] shows that it is highly laevorotary;

$$[\alpha]_D = -92.$$

This figure has recently been confirmed by Osborne, who obtained values for two determinations of —91.9 to —92.55, respectively.

Since most laboratories are provided with polariscopes reading in percentages of sugar instead of degrees of circular polarization, it was deemed advisable to use such an amount of flour that percentages on the sugar scale could easily be transposed to percentages of gliadin nitrogen.

After a number of preliminary trials it was found that 15.07 grams of flour yielded an extract with 100 cc. of 70 per cent. alcohol that would show a polarization of from —4 to —7 on the sugar scale, depending upon the gliadin content of the flour used. It was also found that the polariscope reading multiplied by 0.2 gave figures corresponding approximately with the results obtained for the gliadin nitrogen by the method described.

In flour, the chief optically active substance is gliadin. The amount of sucrose and invert sugars in wheat flour, according to Krug and Wiley,[2] does not exceed 0.30 per cent. The amount of non-gliadin proteids soluble in alcohol is small, and not sufficient to affect the polariscope reading to more than a few hundretdths of a per cent. In fact, the combined alcohol-soluble carbohydrates and non-gliadin proteids of the alcoholic solution affect the polarization to only a slight extent. In a number of

[1] Bredermann's *Centralblatt für agricultur Chemie*, **25**, 197 (1896).
[2] U. S. Dept. of Agr., Bureau of Chem., Bull. 13, Pt. 8.

cases where the gliadin proteid was precipitated, the non-gliadin rotary bodies showed a reading of less than 0.20 per cent. on the sugar scale, or 0.04 per cent. on the gliadin nitrogen scale. In case extreme accuracy is desired, the gliadin can be precipitated perfectly by mercuric nitrate, and corrections made for non-gliadin rotary bodies. Ordinarily, however, this is not necessary any more than are corrections for raffinose and dextrose in the testing of sugar-beets.

Results obtained with the polariscope compare favorably with those obtained in the way described, from the nitrogen content of the solution. In the following table a few comparative results are given:

No.		Gliadin N, Kjeldahl method.	Gliadin N by polariscope.
1.	Freshly ground spring wheat flour	1.12	1.10
2.	Spring wheat flour, 4 months old	1.05	1.08
3.	" " " 8 " "	1.13	1.10
4.	" " " 12 " "	1.08	1.06
5.	Freshly ground winter wheat flour	1.02	1.04
6.	Winter wheat flour, 4 months old	1.01	1.08
7.	" " " 8 " "	1.03	1.00
8.	Freshly ground winter wheat flour	1.07	1.10
9.	Winter wheat flour, 4 months old	1.03	1.10
10.	" " " 8 " "	1.02	1.08
11.	Spring wheat patent flour	1.22	1.20
12.	" " " "	1.28	1.31
13.	" " " "	1.16	1.16
14.	" " " "	1.27	1.29
	Average	1.10	1.12

(Credit is due Mr. Ralph Hoagland for assistance rendered in the above analytical work.)

The average gliadin content of the fourteen samples as determined from the analysis of the alcoholic solution was 1.10 per cent., and as determined by the polariscope, 1.12. Reducing the average polariscope reading of —5.6 to degrees of circular polarization and substituting the values in the formula

$$(\alpha)_D = \frac{-\alpha}{pl}$$

(in which α represents the reading observed, p the weight in grams of gliadin in 1 cc., and l the length of the tube in decimeters) would give a specific rotary power of about —90, approximately the specific rotary power of gliadin.

Briefly described, the method proposed for the determination of gliadin by the polariscope is as follows: Weigh 15.97 grams of flour into a flask and add 100 cc. of 70 per cent. alcohol. Shake the flask moderately at intervals of a half hour for two or three hours. Leave the alcohol in contact with the flour for from twelve to eighteen hours, at a temperature of about 20° C. Filter the alcoholic solution and polarize, using a 220 mm. tube. Multiply the reading on the sugar scale by 0.2, which gives approximately the per cent. of gliadin nitrogen.

The time of extraction with alcohol can be lessened by the use of a shaking machine and then clarifying the solution by centrifugal action. Excessive shaking is to be avoided, otherwise cloudy filtrates are obtained which cannot be polarized. Some flours, particularly soft wheat flours, frequently give cloudy filtrates. If the alcoholic solutions are kept too long, they become cloudy and cannot be polarized.

The interpretation of results, particularly as to the amount of gliadin which a sample of flour shall contain for good bread-making purposes, is a separate feature of the problem of testing wheat and flour for commercial purposes. As yet, only a limited number of gliadin determinations are available, and only tentative standards are possible. In general, it can be said that flour of good quality should contain 12 per cent. of total proteids ($N \times 6.25$), or about 11 per cent. protein ($N \times 5.7$), and that from 55 to 65 per cent. should be in the form of gliadin. It is believed that the method as here proposed of determining the gliadin content of flour by means of the polariscope will be found both rapid and accurate, and particularly applicable where large numbers of determinations are to be made.

UNIVERSITY OF MINNESOTA,
MINNEAPOLIS, MINN.

THE HYDROLYSIS OF MALTOSE AND OF DEXTRIN BY DILUTE ACIDS AND THE DETERMINATION OF STARCH.

BY WILLIAM A. NOYES, GILBERT CRAWFORD, CHARLES H. JUMPER, EDGAR L. FLORY, AND ROBERT B. ARNOLD.[1]

Received December 10, 1903.

The method of determining starch in common use consists in converting the starch into a mixture of maltose and dextrin by

[1] The work here described formed the basis for theses which were presented for the degree of Bachelor of Science at the Rose Polytechnic Institute by Mr. Crawford in 1901, by Messrs. Jumper and Flory in 1902, and by Mr. Arnold in 1903.

means of diastase, followed, after filtration, by hydrolysis of this mixture to glucose by means of a dilute acid. The time required for the hydrolysis of maltose has been determined empirically by finding the length of the time necessary to give a product which shows a maximum reduction of Fehling's solution.[1]

So far as we are aware no one has ever determined the rate of hydrolysis for maltose and dextrin under the conditions which obtain in the determination of starch. It appeared to us that a determination of this rate would give valuable information with regard to the length of time required for the hydrolysis. Sigmond[2] has determined the rate of hydrolysis for maltose at temperatures of 63.7° to 83.76°, but these determinations have little value for the purpose in question.

In our early experiments Mr. Crawford followed the hydrolysis of maltose by means of the decrease in rotation occasioned by the change from maltose to glucose. Using a 10 per cent. solution of maltose, to which 10 per cent. by volume of hydrochloric acid (sp. gr. 1.125) was added, and heating on a water-bath for varying times, the following results were obtained:

Time. Minutes.	Rotation. Degrees.	Maltose. Per cent.	Glucose. Per cent.	C.
0	21.07	100.0	0	.....
5	16.7	65.2	34.8	0.0372
15	11.8	26.1	73.9	0.0427
30	9.3	6.1	93.9	0.0404
45	9.0	4.0	96.0	0.0317
60	8.5	...	...	.....
∞ (calc.)	8.53	0	100.0	....
				Average, 0.0380

Time for 50 per cent. hydrolysis (calculated), 7.9 minutes.

" " 90 " " " " 26.2 "
" " 99 " " " " 52.6 "
" " 99.5 " " " " 60.5 "

In the table the rotation for complete hydrolysis is

$$\frac{21.07 \times 52.7}{130.2} = 8.53°,$$

assuming 130.2° as the rotation for maltose containing 1 molecule of water of crystallization and 52.7° as the rotation for

[1] Meissl: *J. prakt. Chem.*, [2], **25**, 124 (1882).
[2] *Ztschr. phys. Chem.*, **27**, 385.

glucose for sodium light. The constant C is calculated by the usual formula

$$C = \frac{1}{t} \log \frac{A}{A - x},$$

in which A represents the change in rotation for complete hydrolysis of the maltose to glucose and x represents the change in rotation which has taken place at a given time.[1] The time for 50 per cent. hydrolysis is calculated by the formula

$$t = \frac{\log \frac{A}{A - x}}{C}$$

in which A = 100 and x is the per cent. assumed as hydrolyzed.

In most of the work, more dilute solutions were used and the determinations were made with Fehling's solution. A large number of experiments were carried through, which, in the end, are treated as preliminary, because they were superseded by others, in which the methods employed were more satisfactory. While probably three-fourths of our time was spent upon experiments of this nature, and many of these experiments gave results similar to those recorded below, we shall make no attempt to describe them, nor shall we separate, in the further description, the work of individuals.

Effect of Heating Glucose with Hydrochloric Acid.—To a solution of pure glucose containing approximately 0.5 per cent., 10 per cent. of hydrochloric acid (sp. gr. 1.125)[2] by volume was added; different portions were heated on a water-bath for varying times, with care that the volume was unchanged, then neutralized and the glucose was determined by Fehling's solution. The results given were obtained by three different observers at considerable intervals of time.

Solution of glucose not heated.....	0.1903	0.1905	0.2016
" " " heated one hour...	.....	0.1913	.....
" " " " two hours..	0.1906	.....	0.2015
" " " " three " ..	0.1918	.....	.....
" " " " four " ..	.....	0.1917	0.2004
" " " " five " ..	0.1897	.....	.....
" " " " six " ..	0.1900	0.1889	0.1942
" " " " eight " ..	.....	.....	0.1993
Average.....	0.1905	0.1906	0.1995

[1] See Ostwald: "Lehrbuch d. allg. Chem.," II, **2**, p. 201.

[2] This corresponds to about 2.5 per cent. hydrochloric acid in the solution heated and is the amount used in standard methods of determining starch.

With a single exception, which is probably accidental, the results vary scarcely more than the probable error of the determination. It is evident that the *reducing* power of the glucose solution, as determined by Fehling's solution, is not appreciably altered by heating with acid. It does not follow that the glucose is not altered. Indeed, some alteration is indicated by the darkening of the solutions on prolonged heating. These results do not altogether agree with those of Meissl,[1] who found a loss in reducing power of about 2 per cent. when glucose is heated with 3 per cent. hydrochloric acid for three hours. Winston[2] found no change in reducing power when glucose was heated with 2 per cent. hydrochloric acid for three hours, but a loss of 3.15 per cent. in eleven hours and of 5.41 per cent. in seventeen hours.

Effect of an Excess of Alkali in Neutralizing a Glucose Solution.—The fact that glucose is extremely sensitive to alkalies is well known and could be predicted from its aldehyde nature, but the important bearing of the fact on the neutralization of glucose solutions, which is incidental to the determination of starch, has not, we think, been sufficiently emphasized. A solution of glucose was prepared and, after adding to different portions of it water, or water and acid, or water, acid and sodium hydroxide in such amounts that the concentration for glucose was identical throughout each series, determinations were made with Fehling's solution. The following amounts of cupric oxide were found:

	I.	II.	III.
Original solution with water	0.2154	0.2168	.....
	0.2136	0.2170	.....
Solution with acid only	.....	.....	0.2148
			0.2140
Solution with acid one-half neutralized	.....	.....	0.2140
Acid four-fifths neutralized	0.2128	0.2158	0.2156
	0.2136	0.2168	.....
Acid exactly neutralized	0.2094	0.2132	0.2110
	0.2150	0.2116	.....
Acid six-fifths neutralized	0.2102	0.1956	.....
	0.2114	0.1986	.....
Acid six-fifths neutralized, immediate	.....	.....	0.2118
Acid six-fifths neutralized, after one-half hour	.....	.....	0.2114
Acid six-fifths neutralized, after two hours	.....	.....	0.2072

It is evident that alkaline and even neutral solutions give low

[1] *J. prakt. Chem.*, [2], **25**, 127 (1882).
[2] *J. Anal. Chem.*, **2**, 152 (1888).

results in comparison with solutions of pure glucose, while slightly acid solutions give nearly correct results. In all the later work, accordingly, we have been careful, in neutralizing, to leave the solution somewhat acid. It is very important, also, that the solution should be *cold* before it is neutralized.

Copper Oxide Factor for Glucose.—In determining the rate of hydrolysis of maltose and dextrin by means of Fehling's solution it was necessary to use a method of precipitation which would apply equally to maltose and to glucose. Allihn's[1] method is not suitable, as he directs to boil two minutes for glucose and four minutes for maltose. Defren's[2] method uses the same length of time for all sugars and was selected as most suitable for our purpose. We carried out the method as follows: 15 cc. of copper sulphate solution (69.278 grams to the liter), 15 cc. of the alkaline tartrate solution (356 grams Rochelle salt and 100 grams sodium hydroxide to the liter), and 50 cc. of water were put into a 300 cc. Erlenmeyer flask. The flask, covered with a watch-glass, was placed on a water-bath for five minutes, 25 cc. of the sugar solution (0.5 per cent. or less) were then added from a pipette and the heating was continued for fifteen minutes. The solution was then filtered on asbestos, supported on a platinum disk in a Soxhlet tube of hard glass. The asbestos was purified as directed by Defren. After filtration, the tube was dried in an air-bath at 150°-175°. It was then attached to a Bunsen pump, heated with a burner and air aspirated through it till the oxidation to cupric oxide was complete.

To determine the copper oxide factor we used a pure glucose (Kahlbaum's), which we recrystallized from alcohol.[3] It melted at 144°-146°.

Glucose.	Copper oxide (CuO).	Copper oxide per gram glucose.	Glucose equivalent.
0.0405	0.1044	2.578	0.3879
0.0623	0.1558	2.501	0.3999
0.0824	0.2014	2.444	0.4091
0.0937	0.2255	2.407	0.4155
0.1008	0.2416	2.397	0.4172
0.1117	0.2627	2.352	0.4252

[1] See Wiley's "Principles and Practice of Agricultural Analysis," Vol. III, pp. 155 and 165.

[2] This Journal, **18**, 751.

[3] Levy: "Anleit. z. Darst. org. Prep.," p. 80.

These values differ very considerably from those of Defren,[1] and differ also, though not as greatly, from those recently obtained by Dr. Rolfe.[2] They emphasize again the necessity for each worker to check his results with Fehling's solution by making determinations with pure glucose.

Hydrolysis of Maltose.—The rate of hydrolysis for maltose was determined as follows: One gram of maltose, containing 1 molecule of water of crystallization, was dissolved in water and the volume made up to 200 cc. Twenty cc. of 25 per cent. hydrochloric acid were then added and portions of 25 cc. each were placed in several test-tubes. The latter were weighed and then placed in a boiling water-bath. It was estimated that three minutes were required for the solution to acquire the temperature of the bath. At intervals, a tube was removed from the bath, cooled, brought back to its original weight by the addition of water, if necessary, neutralized and the amount of copper oxide obtained by adding 25 cc. to Fehling's solution was determined in the manner described above.

The method of calculation will be apparent from the following table:

SERIES I.—0.5 PER CENT. SOLUTION.

Time. Minutes.	Copper Oxide	Per Cent. hydrolyzed.	K.	Per cent. of total copper oxide.
0	0.1418	....	.....	57.49
5	0.1940	49.71	0.0597	78.61
15	0.2256	79.81	0.0463	91.41
30	0.2376	91.24	0.0353	96.27
60	0.2440	97.33	0.0262	98.87
120	0.2475	100.66	.....	100.28
180	0.2448	98.09	.....	98.92
∞ (calc.)	0.2468	100.00	.....	100.00

It should be noticed in this and the following tables that the per cent. of total copper oxide and not the per cent. of hydrolysis is the measure of the accuracy which would be obtained in an actual determination of starch. The result at two hours in this series is doubtless misleading, as an indication of complete hydrolysis was not obtained in any other experiment.

[1] *Loc. cit.*

[2] Private communication. See also this Journal, **25**, 1008.

SERIES II.—0.5 PER CENT. SOLUTION.

Time. Minutes.	I. Copper oxide.	II. Copper oxide.	Average per cent. hydrolyzed.	Average K.	Average per cent. total copper oxide.
0	0.1405	0.1405	....	.....	57.35
6	0.2018	0.1942	55.02	0.0580	76.73
11	0.2132	0.2136	69.78	0.0473	87.10
16	0.2208	0.2240	78.37	0.0416	90.77
21	0.2298	0.2280	84.97	0.0393	93.43
31	0.2370	.....	92.34	0.0373	96.73
61	0.2428	0.2386	95.88	0.0238	98.24
Hours.					
2	.....	0.2396	94.84	.....	97.80
4	.....	0.2398	95.02	.....	97.84
6	.....	0.2410	96.17	.....	98.37
∞ (calc.)	0.2450	0.2450	100.00	.....	100.00

SERIES III.—2 PER CENT. SOLUTION.

Time. Minutes.	I. Copper oxide.	II. Copper oxide.	Average per cent. hydrolyzed.	Average K.	Average per cent. total copper oxide.
0	0.1268	0.1268	0.00	.....	57.74
5	0.1580	0.1610	35.23	0.0378	71.72
10	0.1806	0.1822	58.83	0.0386	82.62
15	0.1960	0.1954	74.25	0.0393	89.11
20	0.2050	0.2070	85.34	0.0418	93.78
30	0.2120	0.2118	91.70	0.0360	96.49
60	0.2174	0.2162	96.98	0.0255	98.72
Hours.					
2	.....	0.2178	98.06	.....	99.18
4	.....	0.2162	96.33	.....	98.45
∞ (calc.)	0.2196	0.2196	100.00	.....	100.00

SERIES IV.—4 PER CENT. SOLUTION.

Time. Minutes.	Copper oxide.	Per cent. hydrolyzed.	K.	Per cent. of total copper oxide.
0	0.1268	0.00	.....	57.74
5	0.1656	42.89	0.0487	75.85
10	0.1892	67.24	0.0485	86.16
15	0.1990	77.80	0.0436	90.62
20	0.2074	86.85	0.0441	94.44
30	0.2154	95.47	0.0448	98.09
60	0.2176	97.84	0.0278	99.09
Hours.				
2	0.2150	95.04	.....	97.86
4	0.2154	95.47	.....	98.09
∞ (calc.)	0.2196	100.00	.....	100.00

An examination of these results shows very clearly that the reaction does not proceed to its conclusion as a normal mass reaction. For from twenty to thirty minutes the values of K do not diverge very widely from the average except for the five- and

six-minute periods and the divergence in those cases may be partly occasioned by the uncertainty in regard to the time required for the solutions to reach the temperature of the bath. At the rate indicated by this constant, 99.5 per cent., or more (see p. 268), of the maltose should be hydrolyzed at the end of one hour. The actual hydrolysis in sixty minutes is found to be from 95.88 to 97.84 per cent. After one hour the amount of copper oxide found decreases in almost all cases. As it is shown above that the reducing power of glucose decreases very slowly indeed, if at all, on heating with acid of this strength, it would seem that a portion of the maltose is converted into some other substance than glucose.

In any case, it seemed evident, from a practical standpoint, that a complete hydrolysis cannot be obtained by this method of heating and that no advantage is gained by prolonging the heating beyond one hour.

A few experiments were made with a 10 per cent. solution boiled over a free flame with a return condenser. The constant was approximately 0.06, which would correspond to a hydrolysis of 99.5 per cent. in thirty-eight minutes.

Experiments were also made with an acid $^1/_5$ as strong. This gave, on the water-bath, a constant of approximately 0.006, and over the free flame, a constant of approximately 0.008, which would correspond, respectively, to 380 minutes and 260 minutes for a hydrolysis of 99.5 per cent. What degree of hydrolysis could actually be reached at the end of such a period was not determined.

Hydrolysis of Maltose at 110.8°.—A number of determinations of the rate of hydrolysis of maltose at a temperature of 110.8° were made by placing solutions, prepared as before, in sealed tubes and heating these by suspending them in the vapor of boiling toluene. The concentration of the hydrochloric acid was the same as in the cases already given, *viz.*, 20 cc. of hydrochloric acid of 25 per cent. were added to 200 cc. of the maltose solution.

0.5 PER CENT. SOLUTION.

Time. Minutes.	Copper oxide.	Per cent. hydrolyzed.	K.	Per cent. of total copper oxide.
0	0.1405	....	.....	57.35
15	0.2414	96.56	0.0975	98.53
30	0.2434	98.47	0.0606	99.34
(calc.)	0.2450	100.00	.....	100.00

2 PER CENT. SOLUTION.

Time. Minutes.	Copper oxide.	Per cent. hydrolyzed.	K.	Per cent. of total copper oxide.
0	0.1268	....	.....	57.74
10	0.2146	94.61	0.1275	97.72
20	0.2186	98.93	0.1033	99.55
30	0.2170	97.05	.....	98.82
45	0.2156	95.39	.....	98.17
60	0.2181	98.23	.....	99.32
120	0.2160	95.84	.....	98.36
(calc.)	0.2196	100.00	.....	100.00
0	0.1268	.....	.....	57.74
3 1/2	0.1909	69.07	0.146	86.93
5 1/2	0.2040	83.18	0.1416	92.90
7 1/2	0.2114	91.15	0.1407	96.27
(calc.)	0.2196	100.00	.....	100.00

The results with a 2 per cent. solution are the mean of two closely concordant series of determinations.

If we assume 0.143 as the constant, a hydrolysis of 99.5 per cent. should, theoretically, be obtained in 16.1 minutes. The hydrolysis is approximately three times as rapid as at 100°. The rate of hydrolysis approximates that required for a normal mass reaction only for about eight to ten minutes. The maximum amount of copper is obtained in from twenty to thirty minutes.

Hydrolysis of Dextrin.—Six series of determinations of the rate of hydrolysis of dextrin were made. The dextrin was prepared by making a moderately thick, homogeneous, and nearly transparent, starch paste. This was then treated with malt at a temperature of 60°-62° for from fifteen to twenty minutes. The solution was filtered, concentrated on a water-bath in a partial vacuum and the dextrin precipitated by adding alcohol (sp. gr. 0.83). The precipitated gum was dissolved in water and reprecipitated several times and after the last precipitation it was rendered pulverulent by treatment with strong alcohol. It was then thoroughly dried in a vacuum desiccator over sulphuric acid. The dextrin still retained 1.6 per cent. of maltose, but the results were corrected for this on the basis of the rate of hydrolysis of the maltose as previously determined. It was assumed, in calculating the results, that 9 parts of anhydrous dextrin should give 10 parts of glucose.

The average for the six series of determinations was as follows:

Time.	Copper.	Per cent. hydrolyzed.	K.
6	0.0560	28.29	0.0242
11	0.0892	45.14	0.0237
16	0.1155	58.45	0.0238
21	0.1349	68.32	0.0236
31	0.1570	79.45	0.0221
61	0.1791	90.64	0.0167
121	0.1875	94.84	0.0114
(calc.)	0.1976	100.00	

If we assume the constant as 0.023, one hour and forty minutes should, theoretically, be required for a conversion of 99.5 per cent.

The rate of hydrolysis is approximately one-half that for maltose. After thirty minutes the rate of hydrolysis falls below that required by the constant of the earlier periods, and it appears improbable that complete hydrolysis could be obtained by prolonged heating. The heating was not continued long enough to establish this point, however.

The Hydrolysis of the Mixture of Starch and Dextrin Resulting from the Action of Malt on Starch.—A sample of commercial maize starch was used for the following experiments. This was analyzed and gave:

	Per cent.
Moisture	12.48
Proteids	0.27
Crude fiber	0.11
Fat	0.04
Ash	0.83
Starch (by difference)	86.27

Several combustions were made and these gave, calculated for the anhydrous, ash-free material:

	Carbon.	Hydrogen.
I	44.05	6.19
II	43.60	6.15
III	44.35	6.12
IV	43.87	6.35
Average,	43.97	6.20

The ash was largely an alkali carbonate. To determine the amount of carbon in it 5.767 grams of the starch were burned, giving 0.0472 gram of ash. After treatment with nitric acid and drying at 175°-200°, this increased in weight by 0.0296 gram, from which it is calculated that the ash contained 0.0056 gram

carbon. This would be 0.11 per cent. of the anhydrous starch, giving a total of 44.08 per cent. carbon in the anhydrous, ash-free material. If we assume the proteids as containing 53 per cent. and the fat 77 per cent. of carbon, the per cent. of carbon in the pure starch is 44.05.

	Calculated for $(C_6H_{10}O_5)_n$.	Calculated for $C_{36}H_{62}O_{31}$.[1]	Found
Carbon	44.44	43.64	44.05
Hydrogen	6.23	6.33	6.20

The results evidently agree much better with the commonly accepted formula than with Nägeli's formula.

Rate of Hydrolysis in 0.5 Per Cent. Solution.—About 1 gram of the starch was weighed into a flask, treated with a little water and mixed well. About 100 cc. of water were then added and the whole was heated to boiling on an asbestos plate. The boiling was continued with constant stirring for about twenty minutes. The flask was then immersed in a bath kept at 55°-60°, 10 cc. of malt extract were added, and the flask and contents kept at that temperature for from thirty to sixty minutes. The malt extract was prepared by digesting 10 grams of ground malt with 100 cc. of water for an hour and filtering. The contents of the flask were then boiled for five minutes, cooled, the volumes made up to 200 cc., and 20 cc. of hydrochloric acid (25 per cent.) added. The rate of hydrolysis was then determined in the manner which has been described for maltose. The original reducing power of the extract of malt used was, of course, determined, and also its reducing power after hydrolysis with hydrochloric acid and the appropriate corrections were made.

Four series were made with periods of naught, five, ten, fifteen, twenty and thirty minutes, and four series with naught and twenty minutes, and one, two, three and four hours. To save space, only the constants and the averages will be given, and all will be combined in a single table.

[1] Nägeli's formula: *Ztschr. anal. Chem.*, **17**, 232.

HYDROLYSIS OF STARCH PRODUCTS. 0.5 PER CENT. SOLUTION.

Time. Minutes.	Constants. 1.	2.	3.	4.	Average per cent. hydrolyzed.	Average K.	Average per cent. total copper oxide.
0	.....	.....	.....	.....	0.0	.....	43.59
5	0.0527	0.0491	0.0540	0.0487	44.46	0.0511	68.71
10	0.0430	0.0412	0.0369	0.0405	60.43	0.0404	78.32
15	0.0346	0.0355	0.0338	0.0362	70.15	0.0350	83.22
20	0.0307	0.0323	0.0296	0.0314	75.96	0.0310	86.44
30	.....	.....	.....	0.0265	83.99	0.0265	91.00
Hours.							
1	0.0204	0.0221	0.0183	.....	93.76	0.0203	96.40
2	.....	.....	.....	.....	91.86	....	95.31
3	.....	.....	.....	.....	91.40	.....	95.00
4	.....	.....	.....	.....	90.32	.....	94.41

Rate of Hydrolysis in 2 Per Cent. Solution.—Two series were made, in which the concentration of the starch was four times as great, with the following results:

Time. Minutes.	Per cent. hydrolyzed. 1.	2.	Average K.	Average per cent. total copper oxide.
0	0.0	0.0	.....	45.62
10	52.27	51.17	0.0316	73.76
20	73.35	74.42	0.0292	85.80
30	86.10	86.75	0.0289	92.61
Hours.				
1	94.73	94.76	0.0213	97.14
2	94.58	96.15	.....	97.47
3	87.04	90.45	.....	93.90

Hydrolysis in 2 Per Cent. Solution at 110.8°.—One series of determinations was made in boiling toluene, as has been described for maltose, with the following results:

Time. Minutes.	Per cent. hydrolyzed.	K.	Per cent. of total copper oxide.
0	....	....	45.78
3 1/2	61.20	0.118	79.04
5 1/2	76.32	0.113	87.15
7 1/2	84.00	0.106	91.31
20	95.40	0.067	97.65
30	97.51	0.053	98.68
60	94.55	....	97.12
120	86.76	....	93.00

In general, the results obtained with the mixture of maltose and dextrin, which is formed by the action of malt upon starch, agree closely with those obtained before by the hydrolysis of maltose and dextrin separately.

Direct Hydrolysis of Starch with Hydrochloric Acid.—This was not directly connected with the remainder of the work, but one series of determinations was made which may be of enough interest to record. The starch, 1.2976 grams, was boiled with 150 cc. of water for a half hour, the emulsion cooled, made to 250 cc., and 25 cc. of hydrochloric acid (25 per cent.) added. The hydrolysis was then followed at 100°, as in the other cases.

Time. Minutes.	Copper oxide.	Per cent. hydrolyzed.	K.
5	0.0742	30.51	0.0316
10	0.1254	51.56	0.0315
15	0.1596	65.62	0.0309
20	0.1830	75.25	0.0303
30	0.2150	88.40	0.0312
Hours.			
1	0.2358	96.96	0.0253
2	0.2376	97.70	0.0068
4	0.2384	98.02	0.0035
(calc.)	0.2432	100.00	.....

CONCLUSIONS.

1. In none of these cases, which we have studied, does the hydrolysis proceed towards its conclusion as a normal mass reaction. In each case the reaction follows the law approximately for a short time and then becomes much slower than would accord with its earlier rate. Sigmond,[1] in following the reaction at 74°, reached a different conclusion, but he carried the hydrolysis to only 73.5 per cent., at most, and depended exclusively on the rotary power in his determinations. It would be interesting to determine whether a more complete hydrolysis than we have obtained at 100° could be secured at the lower temperature.

2. While glucose itself is scarcely affected in its reducing power by heating with a 2.5 per cent. solution of hydrochloric acid, the products formed by the hydrolysis of maltose are of such a nature that a maximum reducing power is reached after about one hour at 100°, or after twenty or thirty minutes at 111°. Further heating causes a quite considerable decrease in the reducing power. The maximum reducing power corresponds to a hydrolysis of 96 to 98 per cent. This reducing power is 98 to 99 per cent. of the reducing power which would be attained on

[1] *Ztschr. phys. Chem.*, **27**, 385.

complete hydrolysis. This agrees closely with the results obtained by Meissl.[1]

There is a pretty clear indication that the hydrolysis is more complete in a 2 or 4 per cent. solution than in the 0.5 per cent. solution. There is also, apparently, a slight advantage in using a temperature of 111° rather than 100°.

3. The rate of hydrolysis for dextrin is about one-half that for maltose. Dextrin also shows the same retardation in the reaction which was found with maltose at 100°. The hydrolysis reaches 90 per cent. in one hour. For a normal reaction of the first order, it should reach 99 per cent. in two hours, but, instead of this, there is a hydrolysis of a little less than 95 per cent.

4. The reducing power of the products obtained in our experiments by the action of extract of malt upon starch indicates a composition of 74 to 78 per cent. of maltose and 26 to 22 per cent. of dextrin. Such a mixture, from the results recorded above, should give, after one hour at 100°, about 96 per cent. of the copper oxide which would correspond to a complete hydrolysis. The amount actually found is slightly greater, being 96.4 per cent. for the 0.5 per cent. solution and 97.1 per cent. for the 2 per cent. solution. While a continuance of the heating beyond one hour increases the hydrolysis of the dextrin, the decrease in the reducing power of the hydrolysis products of the maltose nearly or quite neutralizes the effect at the end of the second hour so that, practically, the maximum reducing effect is reached, at 100°, in about one hour's time.

5. By the direct treatment of maize starch with hydrochloric acid (2.5 per cent.) in a 0.5 per cent. solution we have obtained a hydrolysis of 97 per cent. in one hour and of 98 per cent. in four hours. It is noticeable that in this case the reducing power did not decrease. Solomon[2] obtained a complete hydrolysis of potato starch in three hours under similar conditions. Beilstein[3] states, on Solomon's authority, that rice starch gives nearly 4 per cent. less glucose than does potato starch under these conditions.

6. For the determination of starch we would recommend that, after filtration, 10 per cent. by volume of hydrochloric acid (sp.

[1] *J. prakt. Chem.*, (2), **25**, 124.
[2] *Ibid.*, (2), **25**, 355.
[3] "Handbuch d. org. Chem"., Vol. 1, p. 1084.

gr. 1.125) should be added to the solution resulting from the action of extract of malt on the material under examination. After heating for one hour in a flask immersed in a boiling water-bath, making allowance for the time required for the solution to attain the temperature of the bath, the solution is cooled, enough sodium hydroxide is added to neutralize 90 per cent. of the hydrochloric acid used, the solution made up to a definite volume, filtered on a dry filter, if necessary, and the reducing power determined by Fehling's solution. 100 parts of glucose found in this manner represent 93 parts of starch in the original material. *The chemist should determine for himself, with pure glucose, the ratio between glucose and copper oxide or copper for the solutions and method which he uses.*

THE BEHAVIOR OF URIC ACID IN THE URINE AND THE EFFECT OF ALKALIES ON THE SOLUBILITY OF URIC ACID IN THE URINE.[1]

By Francis H. McCrudden.

Received December 30, 1903.

When urine cools, a precipitate of uric acid, or sodium urate, or a mixture of the two, very frequently occurs. But not all the uric acid precipitates. The cause for this precipitation, and the factors which determine how much uric acid shall remain in solution after equilibrium is reached, have always been points of controversy. The subject is one of very great importance in medicine. Theories of gout and the uric acid diathesis and methods of treatment in these diseases have often been evolved from a study of the behavior of the uric acid in the urine.

At first the precipitation was thought to be due to a simple decrease in solubility on cooling, and that the greater the quantity of uric acid present the larger the precipitate. Later it was supposed that an increase in the acidity of the urine takes place on cooling, changing the sodium urate to insoluble uric acid. Again, the alkaline sodium phosphate was supposed to play the rôle of a uric acid solvent. The quantity of alkaline sodium phosphate present, the ratio between the alkaline and the acid sodium phosphate, the quantity of salts present, the amount of coloring-mat-

[1] Read at the St. Louis Meeting of the American Chemical Society.

ter, and other factors have all been supposed by different authors to have some bearing on the matter. None of the theories have explained the behavior of uric acid in the urine. The effect of alkalies on the solubility of uric acid in the urine has also been the subject of a great deal of controversy, and different experimenters have come to entirely different conclusions.

The view most generally held is that in the warm urine, uric acid is present as sodium acid urate. As the urine cools, the alkaline sodium phosphate changes to acid sodium phosphate, and this latter changes the sodium urate to uric acid. The uric acid is insoluble and therefore precipitates. The fact that when cold urine has stood for several hours the amount of uric acid in solution is very much greater than the solubility of uric acid would lead us to expect, has been attributed to the tendency of uric acid to become colloidal.

This explanation cannot be accepted. His[1] has shown that when a colloidal solution of uric acid is shaken with solid uric acid, the colloid precipitates. When a cold urine is shaken with solid uric acid until equilibrium is reached, there is still, according to Klemperer,[2] more uric acid in solution than the solubility of uric acid warrants.

An explanation of the behavior of uric acid in the urine is offered if we turn to physical chemistry for assistance. The affinity constant, k in the equation

$$\frac{C_H \times C_U}{C_{HU}} = k \text{ is } 0.00000151$$

according to His and Paul.[3] (C_H stands for the concentration of the hydrogen ions, U for the concentration of the negative uric acid ions and C_{HU} for the undissociated uric acid.) C_{HU} is a constant, equal, at 18°, to 0.0001363.[1] Then

$$\frac{C_H \times C_U}{0.0001363} = 0.00000151,$$

or the solubility product[1]

$$C_H \times C_U = 0.00000151 \times 0.0001363 = 206 \times 10^{-12}.$$

[1] W. His, jun.: "Die Harnsäureablagerungen des Körpers und die Mittel zu ihrer Lösung." Vortrag. auf der Versammlung Deutscher Naturförscher und Aerzte in Hamburg. *Therapie der Gegenwart*, Neue Folge, **3**, 434 (1901).

[2] G. Klemperer: "Untersuchungen über die Lösungsverhältnisse der Harnsäure im Urin." Verhandlungen des XX Kongresses für innere Medizin zu Wiesbaden (1902).

[3] W. His and T. Paul: "Physikalische-chemische Untersuchungen über das Verhalten der Harnsäure und ihrer Sälze in Lösungen 1 Abhandlungen." *Ztschr. physiol. Chem.*, **31**, 1 (1900-1901).

In the 1500 cc. of urine daily excreted, there is on the average 0.75 gram uric acid excreted in the form of sodium acid urate. This is 0.5 gram per liter, or, dividing by the molecular weight, about 0.003 gram-molecule per liter. A salt in such dilute solution is almost completely dissociated, so that in an aqueous solution of sodium acid urate of the concentration found in the urine, C_U in equation (1) becomes 0.003. Then

$$C_H \times 0.003 = 206 \times 10^{-12}$$

or

$$C_H = \frac{206 \times 10^{-12}}{0.003} = 6.7 \times 10^{-8}.$$

If 2 grams uric acid per day were excreted, a rather high limit, C_H, would be about 2×10^{-8}. If only 0.1 gram uric acid were excreted per day with the ordinary amount of urine, or if in a diseased condition the amount of urine should increase to 4 liters and only 0.4 gram uric acid were excreted, C_H would increase to 34×10^{-8}. In other words, in an aqueous solution of sodium urate of the concentration of average urine we can have hydrogen ions present in a concentration of only about 7×10^{-8}. With the ordinary variations in the amount of urate present in urine, this figure would vary from about 4×10^{-8} to 15×10^{-8}. In solutions of sodium urate of the concentration of urine in extreme pathological cases, it might vary from 2×10^{-8} to 35×10^{-8}. If the concentration of the hydrogen ions increases beyond the limit set by the equation

$$C_H \times C_U = 206 \times 10^{-12},$$

then undissociated uric acid will form, and precipitation of uric acid will occur.

The average acidity of urine expressed by the concentration of the hydrogen ions is 300×10^{-8} according to Rohrer,[1] and 150×10^{-8} according to Höber and Jankowsky.[2] Rohrer found the value to vary in different urines from 40×10^{-8} to 510×10^{-8}. Höber and Jankowsky obtained results varying from 100×10^{-8} to 1000×10^{-8}. In a very few pathological cases the value was slightly outside these limits. We can see then why uric acid should precipitate from cold urine. The concentration of the hydrogen ions is too great to permit the presence of the large

[1] L. Rohrer: "Die Bestimmung der Harnacidität auf elektrometrischem Wege." Pflüger's *Arch.*, **86**, 586 (1901).

[2] Höber and Jankowsky: "Die Acidität des Harns vom Standpunkt der Ionenlehre." *Beiträge zur chemischen Physiologie und Pathologie*, **3**, 525 (1903).

quantity of negative uric acid ions present, so precipitation of uric acid occurs. The fact that uric acid does not always precipitate immediately from the cold urine is due, as His[1] has shown, to the fact that the insoluble uric acid goes into the colloidal condition and does not precipitate for some time. Even when hydrochloric acid is added to the solution, some of this insoluble uric acid is not precipitated for weeks. Pfeiffer,[2] His,[1] and Klemperer[3] have shown that this colloidal uric acid can be precipitated by shaking the solution thoroughly with solid uric acid.

Klemperer showed that when urine is thoroughly shaken with solid uric acid a variable part, but not the whole of the uric acid present, is precipitated from solution. An explanation of this fact is easily given. The acidity of urine as determined by titration, that is, the "potential acidity," is about 10,000 times as great as the real acidity. As soon as the "actual" hydrogen ions present are used up by titration with alkali, more of the "potential" hydrogen ions present are set free to preserve the equilibrium indicated by the equation

$$\frac{C_H \times C_A}{C_{HA}} = k,$$

where C_{HA} is used to indicate the acid or acid bodies to which urine owes its acidity,—probably chiefly NaH_2PO_4. The same thing occurs when the "actual" H ions are carried out of solution by precipitation as uric acid. If merely enough uric acid disappears from solution to use up the "actual" hydrogen ions present, the "actual" acidity of the solution remains practically unaffected, for immediately more H ions are set free from the undissociated HA until equilibrium is reached.

In the equation

$$\frac{C_H \times C_{HPO_4}}{C_{H_2PO_4}} = k,$$

we know that $C_{H_2PO_4}$ is large in comparison with C_H and C_{HPO_4}. Then for small changes in $C_{H_2PO_4}$ due to setting free of H and HPO_4 to establish equilibrium after disappearance of H on account of precipitation of uric acid, we can consider $C_{H_2PO_4}$ prac-

[1] W. His: "Die Harnsäureablagerung des Körpers und die Mittel zu ihrer Lösung." *Therapie des Gegenwart*, Neue Folge, **3**, 434 (1901).

[2] E. Pfeiffer: "Zur Aetiologie und Therapie der Harnsäuren Steine." Verh. des 5 Kongresses für innere Medizin, Wiesbaden, 1886, p. 444.

[3] G. Klemperer: "Untersuchungen über die Lösungverhältnisse der Harnsäure in Urine." Verhandlungen des 10 Kongresses für innere Medizin, Wiesbaden, 1903, p. 219.

tically constant. We know that on account of the presence of Na_2HPO_4 largely dissociated to Na_2 and HPO_4, C_{HPO_4} is large in comparison with C_H so that for small changes in C_{HPO_4} due to the further dissociation of H_2PO_4 to establish equilibrium after disappearance of the "actual" H ions, C_{HPO_4} may be considered practically constant. If we consider

$$\frac{C'_H \times C'_{HPO_4}}{C'_{H_2PO_4}} = K$$

the initial equation, then after precipitation of a very little uric acid, we have the new equation

$$\frac{C''_H \times C''_{HPO_4}}{C'_{H_2PO_4}} = K,$$

where $C''_{HPO_4} = C'_{HPO_4}$, approximately and $C''_{H_2PO_4} = C'_{H_2PO_4}$, approximately. Therefore $C_{H''} = C_{H'}$ approximately. In other words, after a small amount of uric acid has precipitated, carrying away all of the "actual" H ions, the concentration of the H ions is almost the same as before, so that the solubility constant for uric acid is still exceeded, and more uric acid precipitates. After considerable quantities of uric acid have precipitated, the loss of H ions from the H_2PO_4 will decrease the value for $C_{H_2PO_4}$, and the HPO_4 ions formed at the same time will increase the value for C_{HPO_4}. Then C_H must decrease in order to maintain equilibrium. Obviously a time will come when this decrease in concentration of the H ions and the decrease in concentration of the negative U ions brought about through loss of uric acid by precipitation will be so great that $C_H \times C_U$ will be less than 206×10^{-12}. Then no more uric acid will precipitate.

Let us take the value for normal urine $C_H = 150 \times 10^{-8}$, and the amount of uric acid excreted as 0.75 gram in 1000 cc. urine. Then C_U (gram-molecules of urate per liter) $= 0.003$. Let us suppose that by spontaneous precipitation of uric acid or by addition of alkali, C_H has decreased to 15×10^{-8} or to 0.1, its initial value. Then $C_H \times C_U = 206 \times 10^{-12}$ because $15 \times 10^{-8} \times C_U = 206 \times 10^{-12}$ and

$$C_U = \frac{206 \times 10^{-12}}{15 \times 10^{-8}} = 15 \times 10^{-4} = 0.0014.$$

In this case equilibrium is reached when the acidity of the urine has been decreased to 0.1 of its initial value and 0.5 of the uric acid has precipitated.

Ritter,[1] it will be remembered, found that the equilibrium is reached more quickly, that is, less uric acid is precipitated, when large quantities of Na_2HPO_4 are present than when small quantities of Na_2HPO_4 are present. This is easy to understand. The addition of Na_2HPO_4 means the addition of HPO_4 ions. The formation of H_2PO_4 by the union of even a large part of the H ions present with some of this extra HPO_4 would scarcely affect the total value for H_2PO_4 since H_2PO_4 is so large in comparison with H. Therefore $C_H \times C_{HPO_4} = K \times C_{H_2PO_4} =$ a constant in this case. Then addition of HPO_4 will decrease C_H in the same ratio as C_{HPO_4} increases. Further we know that Na_2HPO_4 is alkaline. That is, a solution of Na_2HPO_4 contains OH ions. (This is due to the fact that the reaction $Na_2^{++} + HPO_4^{--} + H^+ + OH^- = Na_2^{++} + H_2PO_4^- + OH^-$ takes place to some extent.) On addition of a solution of Na_2HPO_4 to one of NaH_2PO_4 the reaction $H^+ + OH^- = HOH$ takes place, thus still further decreasing the concentration of the H ions. Therefore, the value of C_H in the equation

$$C_H \times C_U = 206 \times 10^{-12}$$

will be reached sooner when Na_2HPO_4 is added to the solution, and will necessitate the precipitation of a smaller quantity of uric acid before equilibrium is reached.

The effect of the addition of a small quantity of alkali to a cold urine would be the same as the effect of a slight precipitation of the uric acid. The hydroxyl ions from the alkali would combine with the "actual" H ions in order that the value

$$C_H \times C_{OH} = 0.64 \times 10^{-14}$$

should not be exceeded. But then, just as the precipitation of a little uric acid by carrying away the actual hydrogen ions affects the values in the equation

$$\frac{C_H \times C_{HPO_4}}{C_{H_2PO_4}} = k$$

very little, so the value of C_H would not be much affected by the addition of a little alkali. Therefore, since $C_H \times C_U =$ a constant, and the addition of a little alkali does not change H, U is not changed, so that the addition of a little alkali does not change the solubility of uric acid in cold urine. It has, in fact, been

[1] A. Ritter: "Uber die Bedingungen für die Entstehung harnsäurer Sedimente, ein Beitrag zur Theorie der Gicht." *Ztschr. f. Biol.*, **35**, 155 (1897).

shown by experiment, as we shall see later, that partial neutralization of the acidity of a cold urine by alkali does not give it the power of dissolving uric acid crystals. When, however, enough alkali is added to very decidedly decrease $C_{H_2PO_4}$ and correspondingly increase C_{HPO_4}, C_H is decreased to maintain equilibrium, and when C_H is decreased enough to approach the concentration allowed by the equation

$$C_H \times C_U = 206 \times 10^{-12},$$

then the solubility of uric acid begins to be increased.

With increase in temperature, k increases. C_{HU}, the value for the solubility of the undissociated uric acid, also increases. Therefore,

$$C_H \times C_U = k \times C_{HU}$$

is very largely increased, but since C_U is constant for any given urine, the value

$$C_H = \frac{k \times C_{HU}}{C_U}$$

is greatly increased. In other words, the concentration of the H ions, which can exist in solution with a definite amount of negative urate ions, is increased with the temperature. With increase in temperature there is also an increase in the dissociation of the other weak bases and acids in the urine. But the OH ions from the bases neutralize the H ions from the acids according to the equation $H + OH = HOH$. If the increase in the supply of the OH ions is equal to the increase in the supply of H ions, the actual number of the H ions will remain the same with increase in temperature. In the equation

$$C_H \times C_U = k \times C_{HU}$$

or

$$C_U = \frac{k \times C_{HU}}{C_H},$$

we have, in such a case, k increasing, C_{HU} increasing, and C_H constant. Therefore, C_U must increase; that is, the amount of negative uric acid ions or sodium urate that can remain in solution is greater. Or, to put it more generally, if the increase in concentration of the OH ions is rapid enough to prevent the actual concentration of the C_H ions in any urine from increasing as rapidly as the value for C_H in the equation

$$C_H = \frac{k \times C_{HU}}{C_U},$$

then the solubility of the uric acid will increase with increase in temperature. If the concentration of the OH ions increases faster than the concentration of the H ions, the actual value for the concentration of the H ions will decrease with increase in temperature. In this case, which, as we shall see, is probably the condition in normal urine, the solubility of the uric acid will increase with rise in temperature faster than it will increase in pure water. As the value $C_{H'}$ for the actual concentration of H ions decreases, and the value $C_{H''}$ for the concentration of H ions permitted by the equation

$$C_H = \frac{k \times C_{HU}}{C_U}$$

increases, a point will be reached where $C_{H'} = C_{H''}$. As we pass this point uric acid becomes the strongest acid in the urine, and, in fact, we have proof that, at 37°, uric acid is the strongest acid in the urine.

Tunicliffe and Rosenheim[1] took a set of flasks containing 100 cc. of urine each and containing an excess of undissolved uric acid, added to each 0.2 gram of different alkalies and allowed the solution to remain at a temperature of about 37° C. until saturated. The alkalies used were piperidine, lysidine, and piperazine. These authors found that the amount of uric acid dissolved by each was proportional to the solubility of their respective urates. If there were a stronger acid than uric acid present, we should have the condition described on pages 7 and 8, that is, these alkalies would not effect the solubility of the uric acid. On addition of a little alkali the H ions would disappear to form HOH. Immediately new H ions would be supplied by dissociation of the stronger acid, HA. In the case of warm urine, however, as the H ions disappear, more are supplied by further dissociation of HU. But this decreases the concentration of the undissociated HU. Therefore, more uric acid goes into solution to supply the deficiency.

The precipitation of sodium acid urate in urine is due to the fact that the product

$$C_{Na} \times C_U = k \times C_{NaU}$$

is exceeded. Either a high concentration of sodium salts or a large amount of uric acid might bring about a precipitation of

[1] F. Tunicliffe and O. Rosenheim: "Piperidine as a Uric Acid Solvent, a Comparative Study." *Lancet*, July 23, 1898.

sodium urate. We can see a reason, therefore, for a precipitation of the urate in alkaline urine, a condition which sometimes occurs. A precipitation of both uric acid and sodium acid urate such as we often have in urine will occur when the concentration of Na ions, H ions, and negative U ions is such that the values for the solubility products of both the uric acid and the sodium urate are exceeded.

What now will be the effect of alkali on a urine from which uric acid precipitates while still warm? Obviously, in this case, the solubility product,

$$C_H \times C_U = k,$$

is exceeded even in the warm urine. Uric acid is not the strongest acid in solution. We have, in this case, the condition usually found in cold urine. The addition of a little alkali will not, therefore, affect the solubility of uric acid. Addition of large amounts of alkali will have some effect on the solubility of the uric acid.

By the addition, then, of alkali to a normal urine we should increase the solubility of uric acid in it at the body temperature, and by the addition of considerable quantities of alkali to a urine from which uric acid precipitates while still warm, we should expect to increase its power of dissolving uric acid at the body temperature. As it is the latter case with which we have to deal in the practical therapeutics of uric acid calculi and gravel, we should, for the best results, give as much alkali as it is possible to give without making the urine alkaline. We can see the reason for the apparently contradictory results of different experimenters on the effect of alkali on the solubility of uric acid in urine. The result depends on the temperature, the quantity of alkali, and on the conditions in the urine.

We hope to determine the dissociation constants

$$k = \frac{C_H \times C_{HPO_4}}{C_{HPO_4}} \text{ (at 18°)},$$

$$k_2 = \frac{C_H \times C_{HPO_4}}{C_{H_2PO_4}} \text{ (at 37°)},$$

$$k_3 = \frac{C_H \times C_U}{C_{HU}} \text{ (at 37°)},$$

and to study the "actual" and "potential" acidity of different

urines at 18° and at 37°, their content of alkaline and acid sodium phosphate and uric acid, and the amount of uric acid precipitated on cooling, in order that the condition in urine be made still clearer, and that we may be able to predict quantitatively from the chemical composition and acidity of the urine, the effect of a certain amount of alkali on a urine and the amount of uric acid which will precipitate spontaneously on cooling. We can then, perhaps, do something for those suffering from uric acid calculi and gravel. Later we hope to study the blood and tissue fluids by physico-chemical methods. This rich and unexplored field must certainly offer a good harvest to the physiological chemist. The results will, perhaps, throw light not only on gout but on many other of those diseases which are classed as disorders of metabolism.

CHEMICAL LABORATORY,
MASSACHUSETTS GENERAL HOSPITAL,
BOSTON, MASS.

THE GERMINATION OF BARLEY.

BY ARVID NILSON.

Received December 29, 1903.

ACCORDING to the prevalent theory, the germination of the barley is caused largely by the action of enzymes in the presence of oxygen, moisture, and a suitable temperature.

Of the enzymes contained in the barley, the diastase and the peptase have been most thoroughly investigated. The diastase changes the insoluble starch into soluble sugar, and the peptase is supposed to change the insoluble albumen into soluble, coagulable albumen, albumoses, peptones, and amido-bodies.

Late researches, however, have made the existence of enzymes in the barley rather doubtful, and more than one investigator has failed to detect enzymes in appreciable quantities, even after the steeping of the barley. It is only after the growth is well on the way that the enzymes make their appearance in quantity, and they, therefore, seem to be rather the consequence than the cause of the growth.

I do not thereby deny that the enzymes are indispensable to the germination, but claim that they are not the primary cause of the growth, and that some other agent must be looked for

which releases the energy stored in the barley by the mother plant in the form of insoluble albumen and starch.

This agent which starts the series of chemical changes that constitute the germination is, in my opinion, the lactic acid-producing bacteria, which are always present in the barley grain under normal conditions.

When the barley is steeped, these bacteria are carried by the steeping water under the hull of the grain. They then develop, feeding upon the ready formed sugar of the grain, and splitting it up into lactic acid. The acid thus produced dissolves the insoluble albumen, and evidently in some way or another sets free the enzymes, which then act upon the albumen brought into solution by the acid, changing it from the colloidal state into diffusible amido-bodies, and at the same time changing the insoluble starch into sugar, thereby supplying the germ with digestible food.

That the insoluble albumen of the barley is not brought into solution by the proteolytic enzyme of the barley, that is by the peptase, has been proved by W. Loé, and I have found that the increase of soluble albumen goes hand in hand with the increase of acidity in the barley. I have, however, as yet no experimental proof of the supposition that the acid produces the enzyme from the insoluble albumen molecule, though many indications point towards this conclusion.

It is a well-known fact that the enzymes act only in slightly acid solutions, at least such enzymes as the diastase and peptase of the barley. If ground malt, for instance, is treated with a 0.01 normal solution of caustic soda, in the proportion of about 1 part of malt and 10 parts of solution, the resulting mash shows a very slight alkalinity. But this alkalinity is enough to render the conversion of starch very incomplete, and also to lessen the total amount of albumen, or, in other words, enough to destroy almost all enzymatic action.

If we then take a ten times stronger solution, or 0.1 normal solution of caustic soda, and steep some barley in this solution, it is safe to say that, even if the enzymes are present in small quantities in the barley, they will be put out of action by such a strong alkalinity, and that, consequently, if the enzymes were the starting factors in the growth of the barley, no growth would follow.

The barley becomes dark brown after twenty-four hours' steeping in such 0.1 normal caustic soda, but when it is placed in the growing-box it gradually begins to pale in spots; after a day or two the rootlets appear, and, as the growth proceeds, the barley regains its normal color.

Even a 0.15 normal caustic soda (0.6 per cent. NaOH) will not entirely prevent growth, but higher concentrations destroy the structure of the barley grain, and a solution of normal caustic soda turns it into a jelly in twenty-four hours.

The bacteria, on the other hand, are not affected by solutions of caustic soda of such strength as 0.15 normal. They develop, produce the acid which not only neutralizes the alkalinity, but renders the contents of the barley of a decidedly acid reaction, and makes growth possible.

The addition of a substance detrimental to the enzymes does then not hinder the growth of the barley, as long as this detrimental influence can be neutralized by the action of the bacteria, and since the action of the bacteria under such abnormal conditions precedes the growth, it is very likely to do so under normal circumstances also.

On the other hand, if we interfere with the development of the bacteria without injuring the enzymes, the result is very different.

As a general rule, the living cell is more sensitive to antiseptics than the enzymes produced by the cell. Utilizing this fact, I steeped barley in water saturated with toluene. Water takes up only a small quantity of toluene, and the solutions used always had a surplus of the oil floating on the top.

A steeping of the barley for twenty-four hours in such toluene water effectually stops the growth, and repeated washings of the steeped barley with pure water does not remedy it.

That the toluene has but a slight action upon the enzymes is seen from the fact that solutions of enzymes can be preserved with toluene for several days without losing their strength, and if malt is mashed with toluene water, the conversion of starch to sugar is as complete as when pure water is employed. The total albumen in such wort containing toluene is slightly less than that of a pure water mash, because the lactic acid bacteria are active in the mash with pure water up to a temperature of 50° C.,

producing lactic acid, and, as a consequence, more soluble albumen, whereas all bacterial action is suppressed in the mash with toluene water.

Destruction of the bacteria of the barley grain inhibits, then, the germination, even if the enzymes are left intact.

It is, however, only the start of germination that is checked by toluene. If barley is steeped in water and allowed to grow until the blade begins to show, then the growing barley may be sprinkled with toluene water repeatedly, without any apparent injury to the plant, showing how little the enzymes, once formed, are affected by the toluene.

Since the alkalinity of a 0.1 normal solution of caustic soda does not prevent the germination of the barley, it might be expected that an equivalent quantity of ammonium hydroxide would also be overcome by the acid produced by the lactic acid bacteria. But such is not the case.

If barley is steeped in $^1/_{20}$ normal and even in $^1/_{25}$ normal ammonia for twenty-four hours, the grain acquires the dark color of the alkaline reaction, but when placed in the growing-box it does not pale, nor does it germinate. The lactic acid bacteria are evidently weakened by the ammonia to such an extent that they have not the energy to decompose the sugar of the grain. They may, nevertheless, be coaxed into action, if offered a more suitable medium. When 2 per cent. of cane-sugar is added to the $^1/_{20}$ normal ammonia, in which the barley is steeped, and the steeping is carried on at a slightly higher temperature, for instance, 25° to 28° C., then after a couple of days lactic acid fermentation sets in, and the browned barley turns yellow again. If placed in the growing-box, a few kernels may sprout, but most of them are weakened too much by the long steeping. Though the steeping of the barley in dilute ammonia prevents germination, it does not stop the development of bacteria. If the barley after a twenty-four hours' steep in $^1/_{20}$ normal ammonia is placed in a sterilized flask, closed with a cotton plug, putrefaction of the barley rapidly follows.

There exists, then, in the barley grain more than one species of bacteria, which, of course, might be expected.

In order to gain a little more definite knowledge concerning these bacteria, a few wort-gelatine plates were prepared in the following manner:

Some barley was washed by repeatedly shaking it with distilled sterilized water, two kernels were then rapidly ground in a sterilized mortar with some sterilized water and the mixture made up to 100 cc. After thoroughly mixing, 0.1 cc. of this mixture was run into 10 cc. of liquefied wort-gelatine, and a plate made in a Petri dish. The same process was carried out with 2 kernels of the barley after it had been steeped for twenty-four hours in sterilized water, in a sterilized flask, closed with cotton, and also with 2 kernels after twenty-four hours' growth in the same sterilized flask.

The first plate showed a few colonies, the second a considerably larger number, the third had almost too many to be counted, showing the gradual development and increase of bacteria during steeping and growth. The colonies were of two distinctly different kinds. One kind was formed by bacteria which, under the microscope, appeared as short non-motile rods, and these colonies remained elevated on top of the gelatine plate; the other kind of colonies were formed by bacteria of longer rods with a lively motion, and these colonies sank into the plate, liquefying the gelatine, and formed hollows filled with liquid. This liquid colored red litmus paper blue, and evidently contained ammonia.

The fact that barley steeped in dilute ammonia will putrefy but not grow, would then be explained by the presence of these ammonia-producing bacteria. Such bacteria would naturally not be as sensitive to a small amount of ammonia as the lactic acid-producing bacteria; the former would increase, producing ammonia enough to counteract the acid produced by the latter species of bacteria, thus keeping the barley alkaline and preventing the formation of enzymes.

The germ of death lies then in the barley grain side by side with the germ of life, and outside circumstances decide whether the grain will live or die. Should the barley, for instance, be surrounded in the ground by too much of decaying substances, the ammonia produced would cause the barley to rot instead of grow.

It seems then that the higher plant is still dependent upon that simpler form of life from which it has evolved, and that it rises up from and again falls back into that current of bacterial life

which flows forever, and is self-contained to the same extent as it is original.

WAHL-HENIUS INSTITUTE OF FERMENTOEOGY,
CHICAGO, ILL.

THE DETERMINATION OF TOTAL CARBON IN COAL AND SOIL.[1]

BY S. W. PARR.

Received December 26, 1903.

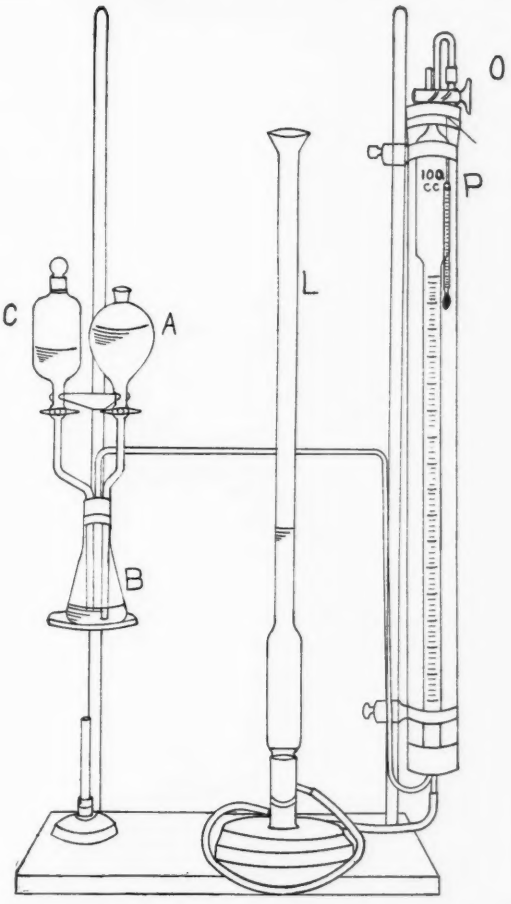
WHERE many determinations of carbon are to be made, the ordinary combustion process becomes a very heavy task. The method here offered was developed in the first instance for technical purposes, more especially in the study of fuel economy, but in practical use it has exhibited a degree of accuracy and a range of service which may give it wider application.

The material employed is the residue from the determination of heat values by means of the calorimeter, recently described by the writer.[2] The combustion of organic material is effected by means of sodium peroxide, the charge being contained in a closed bomb or cartridge surrounded by water. The resulting product, sodium carbonate, together with the excess of sodium peroxide is dissolved in a minimum amount of water and boiled for about five minutes to decompose the peroxide and remove all free oxygen. The carbon dioxide in the residue is determined by volume. To meet the conditions as to solution, volume, etc., the following apparatus has been devised. It has been found of much greater accuracy than various forms of alkalimeters, which have been tried for comparison, and its ease of manipulation makes it preferable to the absorption method, especially for technical work.

The holder A is of 200 cc. capacity and contains sulphuric acid of about 1.4 specific gravity. The flask B is of 125 to 135 cc. capacity. The receptacle C is for the solution of the carbonate. P is a jacketed gas burette with three-way cock at O. To operate, the acid is run in from A, filling B completely, and to the zero mark of the burette at O. Exactly 100 cc. of air at ordinary pressure is measured in the burette and this is forced over into the flask B,

[1] Read at the St. Louis meeting of the American Chemical Society.

[2] This Journal, **22**, 646.



thereby returning the greater part of the acid into A, leaving 25 or 35 cc. in the flask. With the acid cock closed and the cock at O open, the alkaline carbonate is admitted, thus liberating the carbon dioxide gas.

When the volume of liberated gas reaches the limit of capacity of the burette, the cock O is closed, the volume brought to atmospheric pressure by means of the leveling tube L, and after read-

ing, discharged into the air, thus bringing the liquid in the burette to the zero mark at O. The cock is again opened to connect with the flask B. When the liquid from C is all admitted and the sides washed down, heat is applied to B. After boiling a moment, more water is added to C until B is completely filled to the zero point at O. The total volume of gas, minus the 100 cc. introduced to start with, is calculated to carbon at atmospheric pressure and the temperature indicated by the thermometer in the water surrounding the burette.

A correction blank is run in the same manner to determine the carbon dioxide in the sodium peroxide used. This correction factor is calculated to carbon and subtracted from all the tests made with the same lot of sodium peroxide.

Of course, all water used in any part of the operation should be recently boiled and this includes the water used to dissolve the fused residue from the cartridge. It is well to interpose a screen between the lamp and the jacketed burette. Unless the boiling is too long-continued, there is little danger of carrying over any appreciable amount of heat into P. The hand on the connecting tube will tell how far the steam has traveled.

The following table gives the results by this method in comparison with results obtained by means of the combustion furnace and absorption in potash bulbs. One-half gram samples of Illinois coal, oven-dried, were used in the work.

TABLE I.—TOTAL CARBON IN COALS.

No.	Kind.	Gravimetric. Per cent.	Volumetric. Per cent.	Variation from gravimetric. Per cent.
1	Bloomington lump	67.94	67.34	— 0.60
2	Carterville washed, No. 2	74.19	73.32	— 0.87
3	Danville lump	72.40	71.69	— 0.71
4	Elmwood, 3rd vein	72.55	71.84	— 0.71
5	Moweaqua	65.96	65.76	— 0.20
6	Odin pea	65.10	64.62	— 0.48
7	Pana slack	59.29	58.96	— 0.33
8	Ridgely pea	62.85	62.72	— 0.13
9	St. John lump	71.61	71.43	— 0.18
10	Spring Valley washed screenings	65.25	64.80	— 0.45

In the next table Illinois soils were used. The samples and gravimetric factors were kindly furnished by Mr. Pettit, of the Agricultural Experiment Station of the University of Illinois, and I am indebted to Mr. Chas. Edwards, who has worked out

the volumetric results. In this work, 2-gram samples were used, and the amount of organic matter being insufficient of itself to complete the combustion, 0.5 gram of flowers of sulphur was used with each charge.

TABLE II.—TOTAL CARBON IN SOILS.

Sample No.	Volumetric. Per cent.	Average. Per cent.	Gravimetric. Per cent.	Variation from gravimetric. Per cent.
59	3.50, 3.32, 3.71, 3.44	3.42	3.49	—0.05
119	3.23, 3.11, 3.08	3.14	3.24	—0.10
121	0.76, 0.73	0.75	0.68	+0.07
473	1.06, 1.02	1.04	0.91	+0.13
474	0.28, 0.31, 0.31	0.30	0.37	—0.06
475	0.14, 0.08, 0.11	0.11	0.13	—0.02
630	2.00, 2.00	2.00	1.94	+0.06
661	4.25, 4.07	4.16	4.15	+0.01
662	2.69, 2.49	2.59	2.57	+0.02
690	1.32, 1.29	1.31	1.31	—0.00

A sample of oxalic acid gave 19.08 per cent. carbon against 19.04 per cent., the theoretical amount.

UNIVERSITY OF ILLINOIS.

[CONTRIBUTIONS FROM THE UNIVERSITY OF ILLINOIS AGRICULTURAL EXPERIMENT STATION, NO. 11.]

THE DIRECT DETERMINATION OF POTASSIUM IN THE ASH OF PLANTS.

BY EDWARD MURRAY EAST.

Received December 18, 1903.

IN CONNECTION with a large amount of analytical work relating to soil investigations, it has been found necessary to have many determinations made of the elements nitrogen, phosphorus,

and potassium, in foodstuffs, in manure, etc. In making these determinations it was desirable to use short, direct methods, by which the elements required might be estimated without any long, intervening operations, in which elements which seemed to be unimportant in our work are determined.

In the preparation of the ash, on the reliability of which must depend the succeeding phosphorus and potassium determinations, all published methods were carefully considered. The quickest and most satisfactory method used, and a method giving very reliable results, was with the addition of ammonium nitrate to facilitate combustion.[1] The sample was moistened with a 20 per cent. solution of ammonium nitrate and dried on a hot plate. It was then incinerated in a muffle for about two hours at a very low heat. (The muffle had hardly a tinge of red.) The ammonium nitrate furnishes a sufficient amount of oxygen for the complete combustion of the carbon, and at a temperature not sufficiently high to endanger a loss of phosphorus or alkalies, but in some cases leaves nitrates instead of carbonates and chlorides, as was shown by Verdeil.[1] In this method it was found to be saving time and trouble to run three determinations for each sample, using a counterpoise dish and weighing out from 2 to 3 grams, depending upon the kind of sample. One portion is transferred to a weighing bottle, dried at 104°, and the nitrogen determined by the regular Kjeldahl method. The two other portions are transferred to unweighed crucibles incinerated and used for determinations of phosphorus and potassium, respectively.

The methods in use for the direct determinations of phosphorus and nitrogen are all that could be wished in speed and reliability. One man may easily weigh out and complete 40 nitrogen determinations in one day of eight hours, and weigh out, ignite, and complete twenty phosphorus determinations in a like length of time. In the direct determination of potassium, however, difficulties were encountered: First, too much time was consumed in making double alkali determinations which were not needed; second, errors occurred in the determination. In the official method for fertilizers (Lindo-Gladding), there is some danger of mechanical loss of potassium in the evaporation of sulphuric acid. In the official method for alkalies in ashes, the addition of ammonia and ammonium carbonate does not take out

[1] *Ann. Chem. u. Pharm.*, **69**, 89.

all of the barium[1] even with a number of filtrations, and the method is long and tedious.

A method was worked out, however, by which a determination may be finished in one-half the time of the old method, with less danger of loss, giving satisfactory and more closely agreeing results. The procedure is as follows:

Prepare ash from a 2 or 3 gram sample by the above method. Transfer to a beaker with only a few drops of hydrochloric acid and heat to boiling. Add to the hot solution, barium hydroxide solution saturated at 32°, sufficient to precipitate interfering salts. From 3 to 5 cc. are usually enough, providing the hydrochloric acid has been used sparingly. Digest one hour, filter *hot,* and wash with hot water. Precipitate the barium as sulphate by a sodium sulphate solution made up of strength equivalent to the barium hydroxide solution used. Digest five hours, filter, and wash. Evaporate down to about 25 cc. in a platinum dish. Add a drop or two of hydrochloric acid and the calculated amount of chlorplatnic acid needed to convert all the alkalies into chlorplatinates. Proceed as in the Lindo-Gladding method for fertilizers. Transfer all the double salt to the filter, after the first addition of 10 cc. of the ammonium chloride solution. The interfering salts of magnesium and calcium will all be dissolved on the first application. After transferring, five washings of 5 cc. each are sufficient to clear the double salt from impurities; then wash with alcohol, dry, and wash through the filter with hot water, as usual.

This method gave entire satisfaction in speed and reliability. It should be noted that the success of the method depends, in a measure, upon keeping the quantity of reagents used as small as possible. The use of sodium sulphate does away with the use of ammonium salts,[2] and the error which is sometimes caused by driving them off. It also removes all traces of barium as the insoluble sulphate. Sometimes a slight amount of barium goes through the filter; this should not occur, if the liquid has been sufficiently digested; it will, however, be filtered out from the double salt when finally washed through into the platinum dish with hot water. Potassium chlorplatinate is not dissolved in ap-

[1] This Journal, **25,** 490 (1903).

[2] When both sodium and potassium are to be determined, ammonium sulphate is used to complete the precipitation of barium (see this Journal, **25,** 496 (1903)).

preciable amount by the ammonium chloride wash, as was determined by the A. O. A. C.,[1] and the double salt remaining after its use in all cases appeared perfectly pure when examined under a microscope. It may easily be seen in comparing this with the official method that at least two filtrations, and the time and annoyance of driving off ammonium salts are saved. It has also been ascertained that if ordinary care be taken in the laboratory, no ammonium salts will be absorbed.[2] The following table will show how duplicates agree by this method:

Air-dried sample.	Amount taken. Grams.	Per cent. K. 1.	Per cent. K. 2.
Oats	2	0.506	0.506
Corn	2	0.315	0.311
Gluten meal	2	0.245	0.232
Oil meal	2	1.233	1.220
Clover hay	3	1.463	1.452
Corn silage	3	0.809	0.798
Dung No. 1	3	0.485	0.488
Dung No. 2	3	0.510	0.515
Dung No. 3	3	0.585	0.588
Dung No. 4	3	0.477	0.473

NOTE ON A METHOD OF DETERMINING SMALL QUANTITIES OF MERCURY.

By Theodore William Richards and Sidney Kent Singer.

Received January 16, 1904.

In a recent investigation, Richards and Archibald[3] had occasion to detect and estimate small quantities of mercury in the presence of cadmium. The different solution-tensions of these metals at once suggested an electrolytic procedure, but it was found more convenient to conduct the separation with the help of a third metal than with the application of outside electromotive force. Among the many other metals which might have been chosen, copper was selected as the most suitable to precipitate the mercury; because, although its solution-potential is over 0.4 volt greater than that of mercury, it is nevertheless so hard to

[1] 4th An. Con. Bull., **16**, Div. of Chem., p. 44. Also 5th An. Con. Bull., **19**, Div. of Chem., p. 39.

[2] It should be noted that the ammonium double salt is soluble in the Lindo-Gladding wash.

[3] *Proc. Am. Acad.*, **38**, 347 (1902); *Ztschr. phys. Chem.*, **40**, 385 (1902) (?).

dissolve as to be reasonably permanent in aqueous solutions. Since cadmium has a far greater solution-tension than copper (0.75 volt) there could be no danger of contaminating the mercury with cadmium.

Preliminary experiments, made by these investigators, indicated that this method, generally familiar as a common qualitative test for mercury, might also be a useful and convenient one for the quantitative determination of small quantities of the liquid metal; accordingly, the present analyses were undertaken in order to test its accuracy.

Our experiments were made as simply as possible by suspending coils of copper wire, about 1.5 mm. in diameter, in 15 cc. of each of the several solutions containing mercury. The metallic surface had been carefully polished, and cleaned with alkali, acid and water in succession. The coiled wire was found to give better results than the gauze, probably because of the difficulty of cleansing adequately the interstices caused by overlapping wires. When the mercury had been deposited on the copper, the coils were washed with water and alcohol, and dried in a desiccator over calcium chloride. After weighing this amalgamated coil, it was ignited gently in a stream of hydrogen, and then weighed once more. The loss of weight indicated the amount of mercury.

Preliminary experiments pointed toward several necessary precautions. In the first place, it was found that mercurous sulphate or basic sulphates were liable to appear if much sulphuric acid was present, hence nitrates are preferable. An excess of acid is not advisable, because of its independent action on the copper coil. Again, it was found that traces of copper were volatilized with the mercury if the temperature of the ignition was allowed to rise much above the boiling-point of the more volatile metal (350°). Although not necessary, it was found convenient to use two coils, one to take out the great bulk of the mercury, and the other to remove the last traces. As will be seen from the following table, the greater part of the mercury is precipitated in a short time, the remainder requiring many hours. In the analyses recorded below, a solution of mercuric nitrate, containing a known amount of mercury, was used for analysis.

PRECIPITATION OF MERCURY BY COPPER.

No. of analysis.	Time, first coil. Hrs.	Time, second coil. Hrs.	Weight of Hg, first coil. Gram.	Weight of Hg, second coil. Gram.	Total Hg found. Gram.	Total Hg taken. Gram.	Error. Gram.
1	2	2	0.0297	0.0028	0.0325	0.0332	—0.0007
2	3	2	0.0308	0.0015	0.0323	0.0332	—0.0009
3	4	2	0.0311	0.0014	0.0325	0.0332	—0.0007
4	5	2	0.0320	0.0006	0.0326	0.0332	—0.0006
5	6	2	0.0318	0.0009	0.0327	0.0332	—0.0005
6	7	2	0.0326	0.0003	0.0329	0.0332	—0.0003
7	18	2	0.0328	0.0003	0.0331	0.0332	—0.0001
8	18	2	0.0329	0.0001	0.0330	0.0332	—0.0002

This table shows that during two hours 0.9 of the mercury had been precipitated. The introduction of a second fresh coil for two hours more took out four-fifths of the remaining mercury, while leaving the first coil in the solution for the same additional time precipitated half of this residue; these data demonstrate the efficiency of the second coil. Experiment, kindly made for us by Mr. G. E. Behr, Jr., showed that amalgamated copper has essentially the same solution-tension as pure copper, hence the more tardy action of the already amalgamated copper was due merely to the hindering effect of the film of liquid metal in which the copper must dissolve before ionizing. In seven hours, even a single coil precipitated all but 0.6 milligram of mercury, the removal of this last portion requiring more than double the time. The best results would probably be obtained by allowing the first coil to remain four of five hours in the solution, and the second coil to remain there for twenty hours. Stirring would probably accelerate greatly the deposition, and this might be most readily effected by causing the copper coil to rotate. The efficiency of rotating cathodes and anodes in electrolysis has been demonstrated by several experimenters, and this is a parallel case.

HARVARD UNIVERSITY,
December, 1903.

SOME PROPERTIES OF PHENYL ETHER.

BY ALFRED N. COOK.

Received January 4, 1904.

ALTHOUGH many derivatives of phenyl ether have been prepared, the properties of the mother substance have not heretofore

received careful attention. The following properties have been carefully noted by the author.

Solubility.—It is soluble in all ordinary organic solvents. 4.97 parts of the ether are soluble in 100 parts of 87 per cent. alcohol at —10°. At higher temperatures it is very much more soluble. It is soluble in a strong solution of sodium phenolate in water, but is precipitated again on adding considerable water. Water, which has been shaken with phenyl ether, has a strong odor of the substance, and the water obtained from distilling with steam smells *very strongly* of the substance. When it is allowed to stand and cool it deposits long fiber-like crystals, which extend entirely across the containing vessel. It seems, therefore, to be slightly soluble in water, although it has heretofore been considered insoluble in that menstruum.

Boiling- and Melting-points.—The product obtained from distilling aluminum phenolate was washed with caustic soda solution to remove any traces of phenol. It was then distilled seventeen times, discarding the first and last portions each time, crystallized from itself twelve times and from alcohol five times. It then had a perfectly constant boiling-point. The average of several trials which did not vary from each other more than a few hundredths was 258.97° C. after making all corrections. The thermometer was calibrated with water, naphthalene and benzophenone, and required but a small correction. The boiling-point has heretofore been reported at 246° to 254°. These numbers were presumably uncorrected.

The melting-point of the substance, purified as above, was found to be 26.9°-27° C., using a standard thermometer graduated in tenths. On crystallizing again from alcohol several times and distilling with steam, the melting-point was found to be exactly the same.

Crystallization.—Phenyl ether crystallizes from alcohol in large, thin, white plates. On cooling, *per se,* large prismatic crystals were formed, of which the accompanying figure is a fair representative. Some of the crystals lacked one or more faces, but all were hexagonal prisms, apparently belonging to the monoclinic system. The measurement of a specimen gave: Length, 1 cm.; width, 3.5 mm.; thickness, 1 mm. Two other experimenters have stated that the presence of a very small amount of a foreign sub-

stance prevents it from solidifying, but I do not find that this is

Crystal of phenyl ether.

true of phenyl ether any more than with liquids ordinarily. This would also be contrary to now well-known physical-chemical laws.

Volatility.—0.6 gram when heated in a watch-glass on the water-bath lost nearly 0.2 gram in twenty minutes. A small quantity exposed in a beaker at room temperature gradually lost in weight and in six months had almost entirely disappeared. When dried over sulphuric acid the solid ether volatilizes and the acid becomes very much blackened.

Specific Gravity.—The following table gives the specific gravity of the liquid phenyl ether at different temperatures, determined with the Westphal balance.

Temperature. °C.	Specific gravity.	Difference.
40	1.0535	0.0047
35	1.0582	0.0047
30	1.0629	0.0048
25	1.0677	0.0047
20	1.0724	0.0049
15	1.0773	.....

The specific gravity of the liquid ether, determined with the pycnometer at 20°, was 1.0728, and of a specimen that had solidified, 1.1508 at 10.75° C.

Other Properties.—It is oily in character. It has no taste at first, but after a few moments it gives a burning sensation to the tongue and lips. When prepared from aluminum phenolate it was very fluorescent until thoroughly purified. When purified by distilling with steam it is not altered in the light, otherwise it gradually assumed a deep yellow color.

It burns with a smoky flame, liberating a large amount of soot. As has previously been noticed, it has the odor of geraniums, but when hot it has a marked sweetish odor. A teaspoonful administered to a full-grown cat caused frothing at the mouth and considerable discomfort apparently in the throat and stomach, probably due to a burning sensation, but in half an hour the animal was apparently in an entirely normal condition.

MORNINGSIDE COLLEGE,
SIOUX CITY, IA.,
September 21, 1903.

THE MELTING-POINTS OF SOLID CHLOROFORM, TOLUENE AND ETHER.

By E. H. Archibald and D. McIntosh.

Received January 18, 1904.

During the course of an extended investigation on the properties of liquefied gases, we found it necessary to construct some low constant temperature baths. After a number of experiments we came to the conclusion that the melting-points of several pure organic substances were extremely satisfactory for our purpose.

Accordingly, we have determined the melting-points of solid chloroform, toluene and ether, with a fair degree of accuracy by means of the hydrogen thermometer, correcting the observed results according to the methods so well worked out by Travers.[1]

Purification of Material.—Two samples of Merck's chloroform were purified by shaking with water and treating with sulphuric acid; each sample distilled steadily at 60.4° C. under a pressure of 755 mm. of mercury. The toluene used was a sample of Merck's, which had been thoroughly dried with sodium; it distilled between 110.2 and 110.6 under a pressure of 765 mm. Ether, which had been standing over sodium for several months, was distilled; it boiled between 34.2° and 34.7° under a pressure of 757 mm. A second sample was dried by means of phosphorus pentoxide; it distilled between 34.3° and 34.6° under a pressure of 755 mm.

The liquid, whose freezing- or melting-point was to be determined, was poured into a large test-tube, which surrounded the hydrogen thermometer, so as to completely cover the bulb. The liquid was then slowly cooled by means of solid carbon dioxide and ether, or liquid air, being stirred vigorously meanwhile. While the substance was solidifying, the hydrogen thermometer remained practically constant, at least until nearly all the substance had been frozen. The melting-points were determined by surrounding the bulb of the hydrogen thermometer with a pasty mixture of solid and liquid in a vacuum vessel; with vigorous stirring the chloroform and ether melted quite sharply; in the case of the toluene the melting-point did not seem to be sharply defined.

[1] Travers: *Phil. Trans. Roy. Soc.*, **200 A.**, 105.

Chloroform.—The melting- and freezing-points were identical, namely: —63.2° C. This result is probably correct to 0.2°. Berthelot[1] gives —70° C.

Ether.—The melting-point was found to be —117.6° C., which is probably accurate to 0.3°. Olzewski[2] gives —117.4° C. Ladenburg and Krügel[3] found—113.1 C.

Toluene.—The melting-point varied between —97° C. and —99° C. Ladenburg and Krügel found 93.2° C.

A well-stirred mixture of solid carbon dioxide and ether gives a bath having a remarkably constant temperature of about —79.5 C., under normal pressure; by reducing the pressure over this mixture, by means of a good water-pump, constant temperatures down to —103° C. can be obtained.

MACDONALD CHEMISTRY AND MINING BUILDING,
MCGILL UNIVERSITY,
MONTREAL.

ON TRISULPHOXYARSENIC ACID.

[PRELIMINARY NOTICE].

BY LEROY WILEY MCCAY AND WILLIAM FOSTER, JR.

Received January 29, 1904.

BY THE action of magnesium oxide on freshly prepared arsenic pentasulphide suspended in water, we have obtained a solution from which, after removing the dissolved magnesium with sodium hydroxide, we have been able to isolate the tertiary sodium salt of trisulphoxyarsenic[4] acid.

We simply add alcohol to the well-cooled solution, then lower the temperature still further, whereupon feathery crystals gradually separate out, which, on standing[5] in contact with the liquid, pass into fine fern-like forms. By recrystallization in the presence of a small quantity of sodium hydroxide, the salt is obtained pure.

When filtered off, washed with 50 per cent. alcohol and dried

[1] Berthelot: *Bull. Soc. Chim.* [2], **29**, 3-4.

[2] Olzewski: *Wiener Monatsh. Chem.*, **5**, 37.

[3] Ladenburg and Krügel: *Ber. d. chem. Ges.*, **33**, 637.

[4] See the recent work of Foster: *Ztschr. anorg. Chem.*, **37**, 64 (1903).

[5] After adding the alcohol, the flask with its contents is put in the ice-box for about twelve hours.

quickly, by pressing between filter-paper and by fanning, the salt is pure white. Even when impure, it has but a faint yellowish tinge.

When dissolved in water and tested in the cold with a few drops of Weinland's reagent,[1] the solution remains clear and colorless. This serves to distinguish it from the sulpho-salt. Upon standing or upon heating, the solution becomes yellow, and sulphide of antimony separates out.

If a dilute solution of the compound is rendered strongly acid with hydrochloric acid, thoroughly shaken and then filtered, a clear filtrate is obtained which, after boiling for a few moments, becomes only faintly turbid.

By making a similar test with an equal quantity of sodium disulphoxyarseniate ($Na_3AsO_2S_2 + 11H_2O$) of the same dilution, the filtrate, upon boiling, becomes rapidly and strongly cloudy. In both cases hydrogen sulphide is evolved.

A fairly dilute solution of the salt treated with a solution of barium chloride gives a pearly precipitate which closely resembles barium disulphoxyarseniate, but it forms much more slowly than the latter. The precipitate is most probably barium trisulphoxyarseniate.

By dissolving 0.03 gram sodium disulphoxyarseniate in 10 cc. water, and an equal quantity of trisulphoxyarseniate in an equal volume of water, and testing each of the solutions with barium chloride, there is formed almost instantly a heavy precipitate of barium disulphoxyarseniate, while the barium trisulphoxyarseniate appears only after vigorous shaking and the lapse of some moments, and in exceedingly small quantity.

Evidently barium trisulphoxyarseniate is much more soluble in water than barium disulphoxyarseniate.

The yield of sodium trisulphoxyarseniate is highly satisfactory. In several operations we have succeeded in preparing more than 30 grams.

The first analysis below was of the first crop of crystals prepared by direct precipitation with alcohol; the second was of the recrystallized salt.

[1] *Ztschr. anorg. Chem.*, **26**, 327 (1901).

	Calculated for $Na_3AsOS_3 + 11H_2O$.	Found. I.	II.
Sodium	15.22	15.58	15.88
Arsenic	16.50	16.71	16.78
Sulphur	21.16	20.26	20.70
Oxygen	3.52	4.26	3.48
Water	43.60	43.19	43.16
Total,	100.00	100.00	100.00

In another case the salt obtained by direct precipitation with alcohol contained 20.80 per cent. sulphur. After the first recrystallization, the sulphur was 21.31 per cent.; and after the second 21.25 per cent., which is very nearly the theoretical value. Sodium trisulphoxyarseniate effloresces rapidly in a hot room; therefore, the crystals should be dried as speedily as possible.

We expect to publish a more complete account of this interesting acid in the near future.

PRINCETON, N. J.,
January, 20, 1904.

REVIEWS.

Recent Work in Biological Chemistry.

By P. A. LEVENE.

THE greater part of cell and tissue constituents is of proteid nature. The conception of protoplasm was always, in a way, associated with that of living proteids. It is, therefore, natural that the efforts of biological chemists for years were directed toward the study of the chemical nature of proteid material. Through these efforts it was established that in the cell the majority of proteids occur in a more or less intimate combination with various substances. The groups binding the proteids in tissues were designated by Kossel as "prosthetic" groups. Until recently, the knowledge of the chemical nature of either of these two groups of the complex molecule of a combined proteid was very limited. However, the work done during the last few years has added much to our knowledge of the subject.

It has been known that both the simple proteids and the prosthetic groups yield, on hydrolysis, certain simple chemical bodies. But no information as to the manner in which the simple substances combined in order to form the complex molecule of proteid, was obtained.

The work of Drechsel, Miescher, Kossel, Schulze and Emil Fischer on hydrolytic cleavage of proteids has resulted in the dis-

covery of many new substances contained in the proteid molecule, and the synthetical experiments of Emil Fischer have elucidated to a great extent the manner in which the amino acids combine in the proteid molecule.

Before the experiments of Drechsel, monoamino acids were known to result on hydrolytic decomposition of proteids. The monobasic acids of that group known to be present in the proteid molecule were glycocoll, alanine, aminovalerianis acid and leucine. Of the dibasic acids of this group, glutamic and aspartic acids were isolated, and only one oxyamino acid, serine, was shown to be present in the proteid molecule. The methods for isolating the individual amino acids from the decomposition products were so unsatisfactory that only a few of the enumerated acids could be obtained on decomposition of every proteid. The chief difficulty in separating the acids lay in the similarity of their salts in regard to their solubility. Their separation, however, at present is greatly facilitated, chiefly owing to the efforts of Fischer. In the course of a study of the different compounds of the acids, Fischer observed that the ethyl esters of the individual amino acids, if distilled, boiled at diminished pressure, at distinct temperatures, the esters of the lower acids having a low boiling-point. Thus it was made possible to separate amino acids by means of fractional distillation at low pressure. The work was facilitated further by an improvement in the method of transforming the hydrochloric salts into the free esters; and further, Fischer made it possible to individualize the different acids by means of their phenyl isocyanide compounds, and by means of their β-sulphonaphthaline compounds. With these new methods a systematic study of the products of hydrolysis of casein, egg albumen, fibrin, gelatine, keratine, oxyhemoglobin, serumalbumin and edestin was undertaken by Fischer and his students. By them it was etablished that most proteids contain in their molecule amino acids with 2, 3, 4, 5 and 6 carbon atoms. It was also shown that some proteids contain little of the lower acids, while others, on hydrolysis, yield chiefly glycocoll and alanine. It was also demonstrated that the hydroxyamino acids, like serine, occur more frequently than had been known. An amino acid of the pyrrol group was demonstrated in all the analyzed proteids and also a hydroxy acid of the same group. Aspartic and glutamic acids were isolated from the products of hydrolysis of all proteids. Also phenylalanine was proved to be a constant component of the proteid molecule.

Besides the monoamino acids, the proteid molecule also contains diamino acids. They were discovered among the products of hydrolysis by Drechsel. The work on these substances was continued by Kossel and Schulze and their students. The results of their work was reviewed by the author in this Journal,

22, 604, and only the investigations that have appeared since will be discussed in this article.

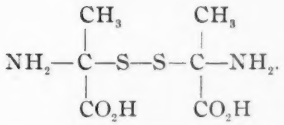
Two diamino acids are known to be present in the proteid molecule, diaminovalerianic and diaminopropionic acids. The former generally appears in the form of a base, arginine. Schulze and Winterstein obtained arginine synthetically from ornithine and cyanimide, and thus have established its nature as a guanidine derivative, namely: guanidine aminovalerianic acid. And Fischer synthetically obtained ornithine and lysine, and thus explained their chemical nature as α,δ-diaminovalerianic acid and α,ε-diaminocaproic acid, respectively. During recent years, nitrogenous substances, belonging to other groups, have been discovered among the cleavage products of proteids. Thus Hopkins and Cole succeeded in preparing a pure "Tryptophan," which they regard as skatolaminoacetic acid. Also Baum and Swain have described a substance of the indigo group and named it skatosine.

By the work of S. Fränkel it has been made probable that there is present in the proteid molecule a base of the pyrimidine group. The base histidine has been generally classified with the diamino acids, the "Hexonbases" of Kossel; according to Fränkel, it is a pyrimidine derivative.

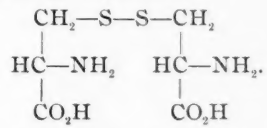
Besides carbon, hydrogen, nitrogen and oxygen, the proteid molecule contains also sulphur, but our knowledge of the form in which the element is present was very limited. It was known that one part of the sulphur of the proteid molecule could be split off by aid of alkalies in the form of hydrogen sulphide and that the other part of the sulphur could not be split off by treatment with the same reagents. Thus it was assumed that the proteid molecule contains its sulphur in two different forms. Attempts to gain better knowledge of the sulphur of the proteid molecule for a long time remained futile. They all, however, corroborated the older observation, and also have established that the two forms of sulphur compounds were present in various proteids in different proportions. During very recent years, however, important work showing the nature of the sulphur-containing substance of proteids, which, on treatment with alkalies, breaks off its sulphur in form of hydrogen sulphide, has been done.

A substance of a similar nature was first observed as a product of abnormal metabolism, and was named cystine. A substance with the elementary composition of cystine was discovered among the cleavage products of proteids.

The chemical nature of the original cystine was explained by Baumann and his co-workers. They showed that it was a derivative of pyrotartaric acid, having the following composition:



Baumann, however, assumed that cystine was not a primary cleavage product of proteids. He based his view on the work of Suter, who failed to detect the substance on hydrolytic cleavage by means of mineral acids. On one occasion Suter, on decomposition of a proteid, found thiolactic acid, and in this Baumann saw a corroboration of his views on the chemical nature of cystine, and also of his view on the presence of cystine in the proteid molecule. K. A. H. Mörner, and later Embden, however, succeeded in obtaining cystine on cleavage of many proteids, and Friedmann demonstrated that cystine thus obtained differs from the one occurring in urine in pathological condition. The proteid cystine has the following composition:



Thus it is related to serine, and might be, as suggested by Friedmann, the mother substance of taurine, which is a normal constituent of bile. This view was very recently corroborated by v. Bergmann, who showed that the production of taurine in the organism increased on feeding with cystine.

It is seen from this summary of the work on the cleavage of proteids that the components of thin molecules are very numerous, and still it is generally admitted that the knowledge of them is not complete. However, even at this stage of our knowledge, attempts have been made to ascertain the way in which the various components are grouped in the proteid molecule.

It has been known from the work of Kühne and his pupils, Chittenden and Neumeister, that on digestion with proteolytic enzymes proteids undergo gradual transformation into proteoses and these into peptones. The relation of the mother substance to the proteid molecule had not been definitely established. Theoretically there were two possibilities: The proteid molecule is a condensation product either of the various albumoses, or of the simple crystalline substances. In the latter case its transformation into albumose could be explained by a gradual losing of some of the crystalline substances. The question, thus, was whether the various albumoses were totally different in their composition, or whether they could be transformed one into another. The older writers characterized individual albumoses chiefly by their solu-

bility and by their behavior toward different mineral salts. They distinguished, however, two groups of digestion products, the anti- and the hemi-groups, and the proteid molecule was supposed to consist of the two moieties. The point of distinction between the two groups lay in the fact that the anti-group could not be hydrolyzed by proteolytic enzymes into simple crystalline components. These problems were the subject of numerous investigations during recent years.

The old methods of Kühne were improved by Hofmeister, and a systematic separation of the proteoses and peptones was carried out in his laboratory, chiefly by Pick and by Zunz. These workers succeeded in isolating a greater number of proteoses than had been known. They demonstrated further that the various fractions differed not only in their solubility and elementary composition, but also in their behavior towards certain reagents. Thus, one fraction was characterized by the intensity with which it responded to the furfural test; another was individualized by its power to decompose lead acetate into the sulphide upon heating with an alkali; again, a third fraction failed to form indol on fusion with potassium hydroxide. It was inferred from this that the albumoses of the first fraction contain much carbohydrate, that those of the second contain much cystine or an analogous substance, and that the albumoses of the third group lack in their molecule the substances of the indigo group.

Another method of establishing the relationship of the primary digestion products of proteids was to compare the crystalline cleavage products in the various fractions of proteoses. Thus Pick, Hart and Haslam demonstrated that the hetero- and proto-albumose differ by the quantities of basic substances in their molecules, and Levene showed that primary and secondary gelatoses differ in the content of glycocoll in their molecules.

Much attention has been devoted to the question of "anti-peptone." As already mentioned, Kühne designated by that name the part of the proteid molecule that could not be decomposed further by tryptic digestion. New investigations undertaken in Drechsel's laboratory on the nature of peptone, have demonstrated that it contains, besides the biuret-giving substance, also simple crystalline bases, commonly occurring on hydrolysis of proteids. A more thorough analysis of the so-called "gland peptone" was undertaken by Kutscher, who came to the conclusion that the product consists of simple crystalline substances only. He, therefore, cast considerable doubt on the existence of an anti-group in the proteid molecule. This view, however, was disputed by Siegfried. This author succeeded in obtaining a substance with the properties of peptone and having a constant composition, a definite rotation, and other characteristic physical properties. He, therefore, modified Kühne's theory thus: On

hydrolysis of proteids with trypsin the following substances are formed: Amino acids, bases and peptones which cannot be decomposed further by the action of the enzyme. The existence of peptones in the sense of Siegfried was recently demonstrated by E. Fischer and Abderhalden.

On the ground of recent investigations it does not seem improbable that a definite relation similar to the one demonstrated by Fischer for carbohydrates and glycolytic enzymes exists between proteids and proteolytic enzymes. Thus trypsin may exercise a stronger action on the proteids of the pancreatic gland than on any other. The observation of Kossel and Mathews that protamines are not affected by pepsin and do undergo cleavage when acted upon by trypsin, supports this assumption.

The *manner in which the amino acids combine in the proteid molecule* remained absolutely unknown until very recently. It is made probable, especially by the work of E. Fischer, that the acids are combined in the molecule after the type of acid amides. Fischer has succeeded in condensing in this manner various amino acids and designates them as peptides. The polypeptides may be formed on condensation of one or more acids. They all resemble, in a degree, true peptones, and Fischer states that he has succeeded in obtaining a similar substance on a partial hydrolysis of proteids.

Some progress has also been made toward a rational *classification* of proteids. The older classification was based chiefly on their solubility and their relation to mineral salts. No information as to the distinction of their chemical composition existed. The methods of obtaining the basic decomposition products were recently improved by Kossel and Kutscher to such an extent that they can be applied for their quantitative estimation. The method of Fischer made it possible to estimate some amino acids with exactness and others with approximation. By the aid of the new methods, considerable work on the estimation of decomposition products of various proteids has been done in the laboratories of Kossel, Hoffmeister, Fischer, and Osborne, from which the existence of two distinct groups of proteids may be regarded as established. To one belongs those composed chiefly of the lower amino acids, glycocoll and alanine. The other components enter the molecule of these proteids in rather small quantities. To the second group belong proteids with a markedly high content of basic substances. Most proteids approach one or the other of the two groups. Proteids differ also by the preponderance of one or another of their basic components.

One of the most striking discoveries of recent years is the application of a new *biological test for the differentiation of proteids.* It was observed by Tschistowitch, Bordet, v. Dungern, and especially by Meyers, that the serum of an animal that had

received subcutaneous injections of a proteid acquires the property of precipitating that proteid from its solution. It was assumed that the serum contained a specific precipitin. Thus, a serum of an animal that had been injected with egg albumen acquired the property of precipitating only egg albumen. This serum thus could serve to differentiate egg albumen from all other proteids, while, on the other hand, the formation of specific precipitins was regarded as a proof of the chemical individuality of different proteids. It has, however, been demonstrated by Levene, Lemoine and Lavasseur that precipitins do not possess that strict specificity that has been claimed for them. By the aid of the precipitin test, proteids are shown to possess a certain biological relationship. Thus albumins and globulins obtained from one animal, or from animals of the same species, can be precipitated by one precipitin, while all albumins of animals of different species do not form precipitates with a serum active for one of them.

COMBINED PROTEIDS.

In the cell and tissues most proteids occur in combinations with other substances, designated by Kossel as their prosthetic group. Such groups of the haemoglobin, of the nucleoproteids and of the glucoproteids have attracted, in recent years, much attention.

Haemoglobin.—To haemoglobin belongs the most important function of supplying tissues with oxygen. The carrier of oxygen is an iron-containing substance, haematin. Also the color of haemoglobin is due to the same substance. However, our knowledge of its chemical constitution, as well as of its relation to other animal pigments, was rather meager. Through the efforts of Nencki, Kuster, Zaleski, Schwink and Marchlewski, considerable knowledge as to the constitution of the substance, and its relation to other animal chromatins, and to chlorophyl, has been gained. It has been shown that haematin is a pyrrol derivative. Upon treating haematin with strong acids a substance, free from iron, is obtained. According to the work of Küster, Nencki and Zaleski, the substance had the composition of $C_{16}H_{18}N_2O_3$, but in a very recent publication Zaleski claimed that the true composition is $C_{32}H_{38}N_4O_6$. This substance can be reduced by hydriodic acid in the presence of phosphonium iodide into a substance of the composition $C_8H_{13}N$. This oxygen-free derivative shows all the properties of pyrrol and is assumed to be isobutyl pyrrol.

Relationship between haematin and bile pigments was again demonstrated by the fact that haemopyrrol, on exposure to air, is transformed into urobilin. It is also transformed into this substance if injected subcutaneously into the organism of a rabbit. On the other hand, it is known that by means of reduction urobilin is transformed into bilirubin.

The relationship between haematin and chlorophyl was established on the ground of the following observations. A substance analogous to haematoporphyrin was obtained from chlorophyl. It has the composition of $C_{16}H_{18}N_2O$, and accepting the formula of $C_{16}H_{16}N_2O(OH)_2$ for the first, it differs from the blood pigments only by two oxygen atoms. Further, on reduction the phyloporphyrin forms the same haemopyrrol as the blood derivative. The pyrrol nature of haematin may also serve to explain its origin from proteids, since the presence of a pyrrol ring in the molecule of all proteid material is quite certain.

Nucleoproteids.—After haemoglobin the next in importance among the combined proteids are the derivatives of nucleic acid. It was established through the researches of Miescher, Kossel, Lilienfeld and Malfatti, that the chromatin of a cell is a phosphorus-containing proteid, possessing certain acid properties. Substances with the staining properties of chromatin could be extracted from cells and tissues. They are all phosphorus-containing, and possessed, in some degree, acid properties. It has been accepted by biologists that the most important functions of the cell are controlled by its chromatin, and it is natural that the study of the chemical nature of these substances attracted considerable attention. Nucleoproteids of two distinct groups are described. To one group belong the derivatives of a proteid-free nucleic acid of a very complex nature, designated as the true nucleic acid. The substances of the second group are apparently direct derivatives of phosphoric acid, and are known as paranucleoproteids.

These compounds were first described by Kossel, Hammarsten and Milroy. They occur in the unfertilized egg as vitellin and in milk as casein. Comparatively little has been known of their chemical nature. Recently P. A. Levene and C. Alsberg published the results of their investigation regarding the nature of the substance. They were led to the conclusion that paranucleoproteids are derivatives of a paranucleic acid. This is a substance with a fairly constant composition, and probably a protein-ester of phosphoric acid. An identical substance could be obtained from the egg of fowls and from that of fish. E. Salkowski obtained an analogous compound from casein.

The number of researches on the nature of true nucleic acid was considerably greater. They were conducted in the laboratories of Kossel, Miescher, Schmiedeberg, Hammarsten, Osborne and Levene. There are two objects in all these researches, one, simply to find the chemical composition of the acid, the other, to ascertain whether the acids vary in their composition in cells with distinct functions. On hydrolysis of nucleic acid there were obtained phosphoric acid, bases of the purine and pyrimidine groups and carbohydrates, a pentose and possibly a hexose. Of

the purine bases two, namely, adenine and guanine, and three bases of the pyrimidine group, namely, thymine, cytosine, and uracyl, were found. *A priori* it seemed possible that there would exist nucleic acids of different complexity. Bang actually succeeded in obtaining a substance much simpler in its composition than the usual acid. It yielded, on hydrolysis, only phosphoric acid, glycerol and guanine pentose. Adenine and the bases of the pyrimidine group were absent from the molecule of that substance. All the other acids contain pyrimidine bases. There is, however, a marked distinction between the acids derived from the animal and that derived from the plant cell. Most of the acids of the first group form, on hydrolysis, the three named pyrimidine bases, while those of the second group contain only cystosine and uracyl. Thymine was first discovered by Kosel, and its constitution as 5-methyl-2,6-hydroxypyrimidine was established by Fischer and by Steudel. Uracyl, 2,6-hydroxypyrimidine, was discovered in yeast, nucleic acid by Ascoli in Kossel's laboratory; it was then found in the wheat embryo by Osborne and Harris. In the acids of animal origin uracyl was first observed by Levene and then by Kossel and Steudel. Cytosine was discovered simultaneously and independently by Kossel and Steudel and by Levene. Its composition as 2-hydroxy-C-amino-pyrimidine was established by Wheeler. Thus at present a distinction can be made between the acids of animal and of plant origin, but there is no evidence in favor of making a distinction between individual acids of animal or plant origin.

To the third group of combined proteids belong the *glucoproteids.* It is as yet uncertain whether or not all the substances of this class are derivatives of one prosthetic group. The chief obstacle in the way of solving the problem lies in the fact that it is very difficult to remove the proteid from the prosthetic group without breaking it up. Until recent years only one substance of the class was successfully isolated and analyzed. It was obtained by Schmiedeberg from cartilage and designated by him as chondroitinsulphuric acid, and was supposed to consist of sulphuric acid, of a hexosamin, of glucoronic and acetic acids. The other proteids of this class were supposed to be derivatives of a polysaccharide, designed by Landwehr as animal gum.

Both these substances have been the subject of renewed investigation recently.

Attempts to ascertain the nature of the carbohydrate entering the molecule of the prosthetic group of glucoproteids have been rather successful. Through the efforts of Fr. Müller and Neuberg, v. Fürth, Langstein and Steudel, it has been established that in the majority of substances of this group, the carbohydrate is a hexosamin. Müller, v. Fürth and Langstein have obtained it in the form of its benzoyl derivative, which they could then

transform into the hydrochlorate. Neuberg demonstrated the appearance of nitroso saccharic acid on oxidation of some of the glucoproteids with nitric acid, and Steudel identified glucosamine by its phenyl isocyanate derivative. Only in one proteid was the reducing substance shown to be galactosamine by F. N. Schultz and Ditthorn. Recent investigations, however, failed to corroborate the old views of the chemical composition of animal gum and of the chondroitinsulphuric acid. Folin repeated, under the direction of Hammarsten, the old experiments of Landwehr, with the result that he obtained a nitrogenous substance, which he designated mucalbumose, instead of animal gum. Orgler and Neuberg undertook a new study on Schmiedeberg's chondroitinsulphuric acid, and came to the conclusion that it did not contain in its molecule either glucosamine or glucoronic acid. They discovered in it a new hydroxyamino acid. Thus the true nature of the substance remains to be explained. At the same time, the substance has been shown to have a much wider occurrence than had been known. Thus Müller has adduced evidence for the belief that in the mucin the carbohydrate is present in form of an acetyl derivative. P. A. Levene has shown the presence of a substance closely resembling Schmiedeberg's chondroitinsulphuric acid in the molecule of tendomucin, and of another substance of the same group in the spleen. Panzer has assumed that ovarial colloid is also a derivative of chondroitinsulphuric acid.

noAther complex substance yielding, on hydrolysis, glucosamin has been isolated by S. Fränkel from egg albumin and designated albamine. It is probable that the substance had the composition of $2(C_6H_9O_4NH_2)+H_2O$.

Thus it may be regarded as established by the investigations of recent years that the carbohydrate of combined proteids is nitrogenous, that the old conception of animal gum was erroneous, and that in many glucoproteids the carbohydrate is present in form of a complex ester of sulphuric acid.

Of the other cell-constituents, some attention has been given to the study of *lecithin* and *cholesterin*. From the researches of Overton and Hans Meyer, it seems probable that the action of different narcotics is dependent upon the coëfficient of their solubility in water and fatty or lecithin-like substances; and Koch has demonstrated that the antagonistic action of different ions on the life of a cell is to some extent dependent on their power to precipitate the lecithans from a colloidal solution.

As lecithans, Koch designates waxy, hygroscopic substances composed of orthophosphoric acids, nitrogenous groups and of glycerin. He has demonstrated that the ratio of nitrogen to the methyl group varies in individual substances of this class.

During life, cell-constituents undergo constant changes. The mechanism through which the transformation of cell-components

takes place has been the subject of many researches during recent years. It is practically established that most of the chemical reactions occurring in the life of a cell or of an organism are due to the presence in them of enzymes. It was generally known that enzymes are capable of bringing about a decomposition of complex into simple substances, and it was accepted that enzyme action was exothermic under all conditions. The natural conclusion was that they could act only in one direction. Observations, however, have shown that a decomposition of 100 per cent. of the original substance through enzyme action is a very rare occurrence under the most favorable conditions. Most generally the products of enzyme action consist of a mixture of the original substance and of its decomposition products. Recent investigations have demonstrated that this is due, not to a deficient cleavage power of the enzyme, but to the fact that the action of an enzyme is reversible. Thus Hill has stated that the yeast enzyme is capable not only of transforming starch into sugar, but also of transforming glucose into maltose. Emmerling has proved that the product of the reversible action of this enzyme is isomaltose. Cremer has shown that yeast plasma is also capable of forming glycogen from glucose. Hanriot and Kastle and Loevenhart here has demonstrated that lipase also possesses a reversible action, and, according to Emmerling, amygdalin can be formed synthetically through the action of yeast maltase. These discoveries are of very great biological importance as tending to explain the mechanism of the synthetical work of the living cell and organs.

Considerable work has also been done toward the explanation of the nature of individual enzymes.

Of very great biological importance is the enzyme causing coagulation of blood, plasma-fibrin ferment. It is chiefly through the work of Buchanan and Alexander Schmidt that the existence of this substance has been made probable. There are, however, authors who have denied its existence. In recent years Huiskamp has attempted to show that the coagulation of blood is caused not by enzyme action but by the action of nucleoproteids. On the other hand, Bordet and Gengou have succeeded in obtaining, by means of immunization, an antifibrin ferment, and thus have adduced new evidence in support of the theory of Schmidt. Arthus has shown that the coagulation of fluor plasma can be caused only by the ferment. Thus, notwithstanding the work done during recent years in this direction, the subject still remains a matter of controversy.

The proteolytic enzymes also have been the subject of renewed investigation during late years. Attempts have been made to ascertain the chemical nature of the enzymes. Friedlander came to the conclusion that they belonged to the class of nucleoproteids.

That this conclusion was based on insufficient evidence has been shown by Levene. On the other hand, different authors claim to have obtaind extracts from digestive glands, possessing proteolytic power, and at the same time giving no evidence of the presence in them of any proteid material.

The old basis for the classification of the enzymes has been to a great extent modified. They were generally distinguished by the reaction and the medium in which they showed greatest activity. Thus enzymes most active in acid solutions were regarded as belonging to the group of pepsin, and in that of trypsin were classified all those active in alkaline media. The endeavors of recent years have been to classify proteolytic enzymes by the end-products of their digestion. Thus it was found that trypsin may, under certain conditions, accomplish the cleavage of proteids to the crystalline constituents of the proteid molecule, leaving no trace of proteid-like substance. On the other hand, pepsin was supposed to be capable of transforming proteids into peptone. Recently, however, Lawrow and Langstein have demonstrated that the mucous membrane of the gastric wall on prolonged self-digestion also forms the crystalline end-products usual to tryptic digestion. Emmerling has shown, also, that papain is capable of decomposing fibrin to the crystalline products generally obtained on hydrolysis with mineral acids. It thus seems at present that by the end-products of their action proteolytic enzymes do not differ one from another. However, in view of the latest work on intracellular enzymes, this conclusion again needs revision.

A proteolytic enzyme with very peculiar properties has been described by Conheim. It was obtained from the intestinal wall and named erepsin. This enzyme does not affect unaltered proteids, but digests very rapidly proteoses and peptones to their final decomposition products. A very peculiar action of proteolytic enzymes has been noted by Okuneff in the laboratory of Danilewski. Okuneff has observed that soluble peptone subjected to the action of pepsin forms, among other products, a coagulated proteid. Kuraieff has demonstrated also that other proteolytic enzymes possess the same property. A certain analogy between this phenomenon and the reversible action of other enzymes is very suggestive.

A practically new chapter, and yet one of great importance for biology, is that of intracellular enzymes. Theodold Smith and Salkowski have discovered the presence of proteolytic enzymes in surviving tissues. The subject then attracted the attention of many investigators, chiefly Hedin and his co-workers, Hofmeister and his co-workers, especially Jacobi and Conradi and Kutscher The questions investigated have been the most favorable condition for their action, the end-products of their digestion and

their specificity. It has been established that most of them exercise the most effective decomposition in a solution of 2 per cent. of acetic acid. As regards the end-products the following have been obtained: Amino-acids, hexone-bases, purine bases, and pyrimidine derivativs. The results of the author's on the autolysis of different organs vary considerably. This may find an explanation either in the distinct nature of the individual enzymes, or in the fact that the methods employed by different authors were not the same. Regarding the specificity of the intracellular enzymes, Jacobi has made a statement that in distinction from the other enzymes their action is limited only to certain proteids. Of great importance is the observation of Müller, Petri and others, that many pathological formations disappear owing to enzyme action, and Jacobi has demonstrated that atrophic condition of organs may be caused by an increase of the enzymotic action of the organ. The relation between enzyme action and other pathological conditions, known as degeneration, has also been the subject of considerable investigation. Among the intracellular enzymes may be classified also the diastase of the liver and the glycolytic enzyme of the spleen. The existence of the former is again the topic of considerable discussion, and Pick in a recent paper insists on its existence. The presence of a glycolytic enzyme in tissues other than the blood has been demonstrated by Conheim, who also states that the enzymotic action appears only in the presence of pancreatic extract.

The influence of mineral salts on many physiological phenomena has been extensively studied during late years, but the discussion of it belongs rather to the domain of physiology, and will, therefore, be omitted in this place.

REFERENCES.

"Products of Hydrolysis of Proteids."—Abderhalden: *Ztschr. physiol. Chem.*, 37; Beneck and Kutscher: *Ibid.*, 32; Fischer: *Ibid.*, 33, 35; Fischer and Sketa: *Ibid.*, 33; Fischer, Levene and Aders: *Ibid.*, 35; Fischer and Abderhalden: *Ibid.*, 36; Fischer and Dörpinghaus: *Ibid.*, 36; Fischer: *Ber. d. chem. Ges.*, 34 and 35; Fischer and Weigert: *Ibid.* (1902); Fränkel: *Monatsh. Chem.*, 24; Kutscher: *Ztschr. physiol. Chem.*, 32.

"Sulphur Compounds in the Proteid Molecule."—Abel: *Ztschr. physiol. Chem.*, 20; Baumann: *Ibid.*, 20; Baumann and Schnutz: *Ibid.*, 20; v. Bergmann: Hofmeister's "Beiträge," Vol. IV; Drechsel: *Ztschr. Biol.*, 33, and *Centrbl. fur Physiol.*, 10; Embden: *Ztschr. physiol. Chem.*, 34; Friedmann: Hofmeister's "Beiträge," Vols. II and III; Moerner: *Ztschr. physiol. Chem.*, 34.

"Peptone."—Fischer: *Ber. d. chem. Ges.*, 36; Fischer and Abderhalden: *Ztschr. physiol. Chem.*, 39; Haslam: *Ibid.*, 32; Hart: *Ibid.*, 33; Kutscher: *Ibid.*, 25, 26, and 32; Kossel and Mathews: *Ibid.*, 25; Levene: *Ibid.*, 37;

Pick: *Ibid.*, 24 and 28, and Hofmeister's "Beiträge," Vol. II; Siegfried: *Ztschr. physiol. Chem.*, 27, 36; Zunz: *Ibid.*, 27 and 28, and Hofmeister's "Beiträge," Vol. II.

"Biological Test for Proteids."—Bordet: *Ann. de l' Inst. Pasteur*, (1899); Camus: *Compt. Rend. de Soc. Biol.* (1902); Hamburger: *Wien. Klin. Woch.* (1901); Lavassier and Lemoins: *Compt. Rend. de la Soc. Biol.* (1902); Levene: *Medical News* (1901); Meyers: *Centrbl. für Bacter.*, 28; Tchistowitch: *Ann. de l' Inst. Pasteur* (1899); Uhlenhuth: *Deutsch. med. Woch.*, (1900) and (1901).

"Hemoglobin."—Küster: *Ber. d. chem. Ges.*, 29, 30, 33, and *Ztschr. physiol. Chem.*, 28, 29, and 40; Marchlewski: *J. prakt. Chem.*, 61, and *Ztschr. physiol. Chem.*, 36; Nencki and Marchlewski: *Ber. d. chem. Ges.*, 34; Nencki and Zaleski: *Ibid.*, 34, and *Ztschr. physiol. Chem.*, 30; Zaleski: *Ztschr. physiol. Chem.*, 37.

"Nucleoproteids."—Ascoli: *Ztschr. physiol. Chem.*, 31; Bang: *Ibid.*, 26 and 31; Kossel and Neumann: *Ibid.*, 22; Kossel and Steudel: *Ibid.*, 37; Levene: *Ibid.*, 31, 32, 37, 38 and 39; Levene and Alsberg: *Ibid.*, 31; Osborne and Harris: *Ibid.*, 36; Salkowski: *Ibid.*, 32; Wheeler: *Am. Chem. J.*, 29.

"Glucoproteids."—Folin: *Ztschr. physiol. Chem.*, 23; Fränkel: *Sitzungsber. d. Kais. Acad. d. Wiss. Matt. Cl.*, Bd. 107, Abt. II C; v. Fürth: Hofmeister's "Beiträge," Vol. I; Langstein: *Ztschr. physiol. Chem.*, 31; Levene: *Ibid.*, 31; Müller: *Ztschr. für Biol.*, 42; Neuberg and Heymann: Hofmeister's "Beiträge," Vol. II; Neuberg and Wolf: *Ber. d. chem. Ges.*, 34; Panjer: *Ztschr. physiol. Chem.*, 28; Schultz and Ditthorn: *Ibid.*, 32.

"Lecithins."—Koch: *Ztschr. physiol. Chem.*, 36 and 37.

"Enzymes."—Arthur: *J. d. Physiol. and Path.*, 3 and 4; Bordet and Gengou: *Ann. d. l' Inst. Pasteur* (1901); Conheim: *Ztschr. physiol. Chem.*, 33, 35 and 36; Emmerling: *Ber. d. chem. Ges.*, 34 and 36; Hauriot: *Compt. Rend.*, 132; Holl: *J. Chem. Soc.*, 73; Kastle and Loevenhart: *Am. Chem. J.*, 24; Kuraieff: Hofmeister's "Beiträge," Vol. II; Langstein: *Ibid.*, 1 and 2; Lawrow: *Ztschr. physiol. Chem.*, 33; Okuneff: Maly's *J. B.*, 25.

"Intracellular Enzymes."—Conradi: Hofmeister's "Beiträge," Vol. I; Conhein: *Ztschr. physiol. Chem.*, 39; Dakin: *Jour. of Physiol.*, 30; Hedin: *Ibid.*, 30; Hedin and Rowland: *Ztschr. physiol. Chem.*, 32; Jacobi: *Ibid.*, 30, 33, and Hofmeister's "Beiträge," Vol. I; Kutscher: *Ztschr. physiol. Chem.*, 32, 34 and 39; Leathes: *Jour. of Physiol.*, 28.

NOTES.

Cereal Foods.—The examination of a large number of cereal foods, representing the products of forty-three manufacturers, has shown that the foods differed only from the grains from which

they were prepared by a lower content of ash, fiber and fat, and a proportionately higher percentage of protein and carbohydrates, this difference being due to the grains having been decorticated or degerminated or generally both, cereals made from untreated whole grain being identical in composition with the grain.

The difference among the various cereals themselves was found to consist only in the percentages of soluble and insoluble carbohydrates. The cereal foods can be divided into two main classes:

I. Cereals made from the whole grain.

II. Cereals made from prepared grains (decorticated and degerminated). Each of these classes again subdivided into:

1. Raw cereal products.
2. Prepared cereal products—cooked or roasted.
3. Medicated cereal products—containing foreign substances.

The prepared and the medicated products are again divided into:

a. Prepared cereal products.

b. Prepared malted cereal products.

The so-called medicated cereal products, containing spices, sugars, gluten, flours, salt, flavoring extracts, etc., have not been considered, as they only differ from the others by the foreign non-cereal substances added.

It will be seen from this division that the raw cereal can be changed to the prepared product by simply cooking or roasting, and into the third class by treatment with malt or its extract. As malt will not act on raw starch directly, this part of the process generally precedes the other, and often the malting, cooking and roasting are done in one step. The starch is changed into a soluble form by the heat, and into sugar by the malt, and the resulting soluble extract determines the whole difference between different cereal foods. The so-called digestibility of these foods depends on the amount of these soluble carbohydrates, and the same can easily be determined by the action of saliva and pancreatin on the materials. The raw cereal to be fit for human consumption should be boiled for at least one hour. If this is done, the mass will show more soluble carbohydrates than any of the prepared or malted cereals I have examined, two samples excepted. In making comparative tests this must be done. The digestion

tests with the saliva and pancreatin were made at temperatures of 36° to 38° C., the original solutions containing 10 per cent. of the cereals. Soluble substance in solution was determined, then the saliva and pancreatin added. Samples were withdrawn at stated intervals, filtered and the extract in the filtrate determined by direct evaporation on the water-bath.

It was found that the raw cereals, if sufficiently cooked, were as quickly digested as the best malted cereals, more quickly than the prepared cereals and a large majority of the so-called malted cereals.

The physical condition of the cereals being flaked, rolled, granulated, shredded or as flour, had a material effect on the time of digestion, but this was overcome by grinding so as to pass through a 60-mesh sieve. The amount of soluble material before digestion varied:

	Per cent.
Raw cereals	2–8
Prepared cereals	4–23
Malted cereals	4–60

Average analysis of the cereals:

	Raw cereals. Per cent.	Prepared cereals. Per cent.	Malted cereals. Per cent.
Ash	1.3	1.3	1.3
Fiber	0.5	0.5	0.6
Fat	0.7	0.7	0.7
Protein	10.5	10.5	10.4
Carbohydrates, insoluble	82.0	72.0	52.0
" soluble	5.0	15.0	35.0
" " after boiling	38.0	36.0	45.0

It was found that the only advantage the prepared and malted cereals have over the raw cereals is that they come to the consumer ready for immediate consumption, and the preliminary preparation of boiling for one hour or so is not required. The claim that the prepared cereals are pre-digested food applied only to the malted cereals and only so far as part of the starch has been converted. After boiling, the raw cereals are just as digestible as the others. The differences in the time of digestion, with saliva and pancreatin, between a well-boiled raw cereal and a fully malted prepared cereal is so small that the same can be

ignored when determining the relative nutritive ratio and factor of digestibility.

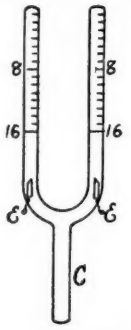
EDWARD GUDEMAN.

CHICAGO, ILL.

A Simple and Inexpensive Apparatus for the Electrolysis of Water.—There is need for an inexpensive, yet reliable piece of apparatus for the electrolysis of water, especially for use in the smaller colleges and high schools. The apparatus, described below, I had made two years ago, and find it the most convenient apparatus for the purpose of any I have seen in the market.

It consists of a U-shaped tube about ¾ inch in diameter, with each arm graduated to 16 cc., and a tube *C* of the same bore and about 4 inches long is fused in at the bend. A platinum electrode *E*, connected to a platinum wire, is fused into each arm of the tube near the bottom.

To operate: The apparatus is inverted and filled with acidulated water, and a piece of wet filter-paper is placed over the end



of the tube *C*, being careful to exclude any bubble of air. Then it is inverted and placed in a vessel of acidulated water. The apparatus may be either clamped in an upright position before attaching the electric wires; or the tube *C* may be thrust through a hole made in a wood cover which fits the tube tight enough to prevent slipping; fill, invert, and place over a beaker of acidulated water with the mouth of the tube below the surface. The wood cover resting on the beaker will hold the apparatus in position. Any glass-blower can make the apparatus.

J. L. BEESON.

GEORGIA NORMAL AND INDUSTRIAL COLLEGE,
MILLEDGEVILLE, GA.

On the Analysis of Zinc Ores.—Through the courtesy of the editor of this Journal, the writer has been allowed to read before its publication the exhaustive paper by W. George Waring on "The Volumetric Determination of Zinc."

In this paper Waring points out, among other sources of error, the danger of loss of zinc by volatilization as chloride when using the Von Schulz and Low method.

The writer has also experienced difficulty in getting good results on some classes of ores by this method and, though he did not learn that he lost zinc by volatilization, finally adopted the following method, which will avoid this danger, as well as effect a more thorough decomposition, and afford an easier method of separating from iron and manganese than the method in general use.

Treat from 1 to 2.5 grams of the finely powdered ore in a flask of about 200 cc. capacity, with 15 cc. of strong hydrochloric acid; boil and effect as complete decomposition with the hydrochloric acid alone as possible, then add 5 cc. strong nitric acid and boil. When the red oxides of nitrogen have been mostly driven off, cool somewhat and add 10 cc. of a mixture of equal parts of strong sulphuric acid and water, boil vigorously, best holding the flask with a holder and moving it over the flame until all the nitric and hydrochloric acids are driven off and dense white fumes of sulphuric acid are evolved. Cool, add 40 cc. water and boil. This treatment will completely decompose most ores, but in case an ore is encountered that is not decomposed, it is necessary to fuse the insoluble residue with sodium and potassium carbonates, dissolve in sulphuric acid, evaporate to fumes, boil with water and add to the main solution.

In a large casserole place 50 cc. of strong ammonia and 25 cc. of water, and add slowly about 2 grams of sodium peroxide. Now, without filtering from the silica, pour the solution of the ore into the peroxide solution. This should be done slowly and with constant stirring. If the precipitate formed here is large, it is best to filter, dissolve the precipitate in hydrochloric acid, reprecipitate with the ammonia-sodium peroxide mixture, filter, wash the precipitate and unite the two filtrates for the zinc determination. When this precipitate is small, however, the amount of zinc carried down is too small to cause any appreciable error,

and it is easiest then to transfer the solution and precipitate to a graduated flask, fill to the mark, mix, filter through a dry paper, and take an aliquot part for the zinc determination. The hydrogen peroxide in the solution may be effectively removed by boiling off about half of the liquid before acidifying. The addition of hydrogen sulphide water after the addition of the acid destroys any trace that may have been left after boiling.

The solution is now ready for the zinc determination, unless the ore contains copper or cadmium, which must, of course, be removed.

PERCY H. WALKER.

CHEMICAL LABORATORY, INTERNATIONAL TEXT-BOOK CO.,
SCRANTON, PA.,
January, 1904.

NEW BOOKS.

ANNUAIRE POUR L'AN 1904, PUBLIE PAR LE BUREAU DES LONGITUDES. 16mo. 732 + 80 pp. Price, 1 fr. 50 centimes. Paris: Gauthier-Villars.

Exactly one-half of this volume is an almanac, with nothing in it of chemical interest. The latter half contains physical and chemical tables, and the reviewer is pleased to be able to modify his criticism of the former volume (1903), and to say that *this* volume is well worth its price to the chemist because of the careful revision and the addition of 13 new tables, the thermochemical tables contributed by Berthelot (47 pages) being alone well worth the cost of the book. These physical and chemical tables will, in future, be published only on alternate years, so that the volumes issuing on the even years will be the only ones of value to the chemist.

JOSEPH W. RICHARDS.

THE TECHNOLOGY OF SUGAR. BY J. G. MACKINTOSH. London: Scott, Greenwood & Co.; New York: D. Van Nostrand Co. 1903. 402 pp. Price, $4.50 net.

A better title would have been "The Technology of Beet Sugar, with Some Supplementary Notes on Cane-Sugar Manufacture." The book will be welcome as a commendable treatise on the technology and history of continental beet sugar-house methods. As a review in English of the classic works of Horsin-Deon and other eminent European sugar-house engineers, it will be useful in the library of the sugar-house and technical school, if only to

inspire a reading of the originals. Evidently the author has no practical acquaintance with beet-sugar work in this country, which has been appreciably modified to suit local conditions, a fact which European experts here seem slow to learn. The use of sulphurous acid ("sulphitation"), practiced widely here and abroad as a vital part of clarification, gets but a passing mention (p. 273).

Following the custom of the foreign treatises, the author gives scant space to cane-sugar technology, although it is his avowed wish, as stated in the preface, to aid those interested in that industry. He gives much of his 50 pages to a discussion of diffusion experiments, but he should know that, aside from any intrinsic advantage of diffusion as an extraction method, prevailing conditions in most tropical sugar regions make that method impracticable. Cane-sugar manufacture, uninfluenced by government paternalism which has so stimulated beet-sugar production and unified methods, exists to-day in all stages of evolution, but in its highest development, as in Cuba or Hawaii particularly, the results have been as successful and the technical attainments as great as in the European industry. It is true, peculiar economic conditions, well worthy of discussion in a sugar technology, have necessitated a sharply defined division of processes between sugar-house and refinery, so that the development in extraction of sugar directly from the plant, being diverted from improvement of product, in late years has been solely in economy of production in field and factory and in increased yield of (designedly crude) sugar.

The improvements of the Stillmans in evaporating and clarifying, in steam economy and general engineering of the refinery and sugar-house, the clarifying process of Deming, the factories of Hedeman and Williams in Hawaii, the cane-handling machinery of Gregg, and many other successful works equally deserving, are worth study in sugar technology.

The Soledad and Trinidad houses in Cuba and the Ewa[1] in Hawaii can be instanced as among those of which each has a yearly output of 10,000 tons of cane-sugar or more, showing a uniformity and economy of production unexcelled anywhere. This has been attained only by high technical development of process

[1] Ewa's output for last crop is reported to be 35,000 tons.

and machinery in house and field, largely by American engineering genius. The mass of data on cane-sugar technology is yet to be collected. It cannot be extracted from the present literature of Europe.

Practically all of the first and last chapters could be omitted to advantage, the subject-matter being far better treated in the text-books on sugar analysis. Some of the methods given are obsolete, and there is much that is unintentionally misleading and misstated. The space could be much better utilized in discussing from a purely technological standpoint the chemistry of beet and cane juice bearing on a comparative study of beet- and cane-sugar technology—simple and well-known principles, so often ignored, even by experts—and the general economic conditions which have been vital in the shaping of the two industries.

Naturally, some misprints have been found, most of them obvious from the context. GEO W. ROLFE.

ELECTROLYTIC PREPARATIONS. Exercises for Use in the Laboratory by Chemists and Electrochemists. BY DR. KARL ELBS, Professor of Organic and Physical Chemistry at the University of Giessen. Translated by R. S. HUTTON, M.Sc., Lecturer in Electrochemistry, Owens College, England. New York: Longmans, Green & Co. Price, $1.60.

This little work of 100 pages is divided into three parts. The source of current, resistances, measuring apparatus and apparatus for electrolysis are clearly and attractively presented in the first part. Thirteen examples from inorganic chemistry constitute the second part. They are arranged so that some of the experiments are made with unattackable and others with soluble anodes. The directions in each case are full and explicit. The third part consists of thirteen examples selected from the domain of organic chemistry. Three of these deal with the electrolysis of organic acids; the remainder consider electrochemical reduction and oxidation methods. Only two examples present the oxidation methods.

The reviewer was on the point of saying that this is regrettable, but instead would substitute that in this particular direction there exist great possibilities, awaiting the attention of those who will devote themselves to a study of this most promising field of research. At present, practical electrochemistry is receiving much

attention at home and abroad, and it would seem the part of wisdom to have the student of chemistry acquaint himself with some of the ordinary procedures in electrochemistry, which he can do by performing the experiments offered in a volume like this of Elbs. Examples in inorganic preparations, in organic preparations, in physico-chemical methods and problems form part of nearly every student's curriculum, and why not include a brief course, such as is here presented, from an equally important and instructive field? Nor should work with the electric furnace be omitted. However, the purpose of this review was not to offer a dissertation on the teaching of electrochemistry, but to indicate the character of the book so that to what has already been said of it may be added: it is well written, accurate in statements and the result of laboratory experience. The author and translator deserve much praise for their labors in the preparation of a suggestive and helpful book. EDGAR F. SMITH.

KALENDER FÜR ELEKTROCHEMIKER SOWIE TECHNISCHE CHEMIKER UND PHYSIKER. 1904. 8th year, 575 pp, with a Beilage of 416 pp. BY DR. A. NEUBURGER, Editor of *Electrochemischen Zeitschrift*. Berlin: M. Krayn. Price, 4 marks.

This is the most complete electrochemical calendar known to the reviewer. It contains the general electrotechnical information found in technical calendars, but includes over 300 pages of chemical and electrochemical data, including information on quantitative analysis by electrolysis, technical electrolysis, electroplating, etc. Over 100 pages are devoted to accumulators. The Beilage contains data on hardness, elasticity, tensile strength and other mechanical data, together with 250 pages on German laws relating to electrochemical industries, including patent laws of the principal countries. W. R. WHITNEY.

UEBER DIE BASISCHE EIGENSCHAFTEN DES SAUERSTOFFS UND KOHLENSTOFFS. VON DR. JULIUS SCHMIDT. Berlin. Gebrüder Borntträge. 1904. iv + 111 pp. Price, 3.20 marks.

This interesting brochure gives a general, connected review of all the recent literature on the basic and tetravalent nature of oxygen and also on the trivalent and basic nature of carbon. Although the work done along these lines is all of very recent date, yet the literature is already sufficiently voluminous to justify the publication of the above-mentioned monograph. One need

but to glance over the pages of this little volume to see what a wealth of suggestion for new work there still is in the old idea of valence. What if we do find that our old notions in regard to the limited and fixed valence of oxygen, and perhaps that of carbon, have to be altered to some extent? By such an extension of our ideas we are enabled now to better correlate many phenomena which previously found no adequate explanation. The subject treated by Dr. Schmidt, to use his own words, "is of equal importance for the organic, inorganic, and physical chemistry. Nor is it devoid of practical interest, for the idea of the tetravalence of oxygen gives us, already, a new insight into the constitution of such important dyestuffs as the oxazines, the thiazines, the pyronines, rosamines, rhodamines, etc."

The book is divided into two parts: About 90 pages are devoted to oxygen, and 15 to carbon. The first part includes, among others, the work of Collie and Tickle on the salts of dimethylpyrone; the investigations of Baeyer and Villiger on the salt-forming properties of oxygen compounds in general; the azoxonium and azothionium salts of Kehrmann; the carboxonium and carbothionium salts of Werner, and, finally, a very readable summary of the several physical-chemical investigations that bear upon this subject. The second part is, of necessity, much smaller; it presents a brief summary of the literature relating to triphenylmethyl, to the salt-like nature of its compounds, the effect of methoxyl groups upon that, etc.

The presentation of the subject is entirely non-critical; the references to the original literature are very full.

M. GOMBERG.

QUANTITATIVE CHEMICAL ANALYSIS. By the late DR. C. REMIGIUS FRESENIUS. Authorized translation of the greatly amplified and revised sixth German edition, by ALFRED I. COHN. New York: John Wiley & Sons. 1904. Two volumes. xii + 780 and xxii + 1255 pp. Price, $12.50.

The preface to the first American edition of this work bears the signature of Samuel W. Johnson and is dated December, 1869, that edition being a translation of the greater part of the fifth German edition. The second American edition bears a preface signed by O. D. Allen, dated February, 1881, and it is there stated that the first volume of the sixth German edition of

the work was in the editor's possession at the time this revision was made. In both of these editions the editors (or translators) have abridged the work somewhat by the omission of certain entire subjects and the curtailment of others, which, in their judgment, treated of methods that were "more curious than useful." Some new material was also inserted by them.

The present issue is a faithful translation of the entire material comprising the two volumes of the sixth German edition, with which has been incorporated the matter inserted by Messrs. Johnson and Allen in the previous American editions, and to which have been added some fifteen or more procedures in the "special part" which have the approval of the translator. Finally, the official methods of analysis, adopted by the Association of Official Agricultural Chemists (Bulletin No. 46 of the U. S. Department of Agriculture) and Dr. Hillebrand's excellent monograph on "Some Principles and Methods of Rock Analysis" (Bulletin No. 176 of the U. S. Geological Survey) are added as Appendix I and II. The table of factors and their multiples, and other values throughout the book, have been recalculated on the basis of the atomic weights of 1902, and both volumes are admirably indexed.

It is rare indeed in recent times that any work has been able to hold an authoritative place in scientific literature through three generations of chemists, all of whom have held it in the highest respect. It is, therefore, only fitting that the very considerable labor which it has cost to prepare an edition in English of this classical work of Fresenius should be duly recognized and appreciated. At the same time, it may be fairly questioned whether the introductory sentence of the translator's preface, to the effect that "the great advances in analytical chemistry since the publication of the previous edition of this work and the introduction of numerous new methods of analysis, and improvements upon older ones, have necessitated a new translation of the most recent German edition" does not lead one to expect a modern, up-to-date treatise, whereas, the first volume of the sixth German edition, of which this is essentially a reproduction in English, bears the imprint of 1875, that of the second volume being 1877-1887. The additional procedures inserted by the translator, while doubtless of value in themselves, do little toward modernizing the

book as a whole, and all who expect to find an up-to-date treatise are bound to be disappointed. Much of the first volume is the unaltered translation of Johnson and Allen; indeed, many of the plates used in this volume are those used in an edition purchased in 1883, while many of the cuts are very badly reproduced, being inferior to those in earlier American editions. It would seem strange, if not inexcusable, to find in a work bearing the date 1904 on its title-page a cut of an old charcoal furnace referred to as "a common combustion furnace" (p. 75, Vol. I), and equally surprising to find no reference to such a determination as that of zinc in the form of phosphate, were it not that this edition must be regarded as a reproduction of an honored (but decidedly old) treatise. As such it is to be commended, and it is very much to be regretted that the publishers have found it necessary to place an almost prohibitive price upon this edition, since it would otherwise doubtless find its way into the library of many of the younger generation of chemists for whom it still has much value as a reference work.

Doubtless the index to the earlier American editions has served to chasten the moral character of many a chemist; nevertheless it is a relief to contemplate the results of the translator's labors in this department. He has earned the gratitude of all users of the volumes. H. P. TALBOT.

A THEORETICAL AND PRACTICAL TREATISE ON THE MANUFACTURE OF SULPHURIC ACID AND ALKALI WITH THE COLLATERAL BRANCHES. By GEORGE LUNGE, PH.D., Professor of Technical Chemistry at the Federal Polytechnic School, Zurich; formerly manager of the Tyne Alkali Works, South Shields. Third edition, revised and enlarged. Vol I in 2 parts—Sulphuric Acid. London: Gurney & Jackson. 1903. 8vo. xxvii + 1214 pp. Price, 2£ 12s. 6d.

The second edition of the first volume of this work appeared in 1891 as a volume of 911 pages. An appendix to Vol. III brought the work down to 1896. Since then the development of the contact process, as well as of the old leaden chamber process itself, has made a new edition necessary, and this the author has prepared with characteristic industry. The volume before us is practically a new book, since much of the material is entirely new and all of it has been carefully rewritten. It is to be hoped that this is not to be, as intimated in his preface, the

last edition to be prepared by Dr. Lunge, who has done so much for the subject. Among Dr. Lunge's qualifications are knowledge of the subject as a manufacturer and teacher, wide acquaintance with technical men on the Continent and in England and America, and an indomitable industry in the collection of material. Among other sources of information, Dr. Lunge speaks of the "United States Census Bulletin No. 210, compiled by Messrs. Munroe and Chatard, and issued in June, 1902, contains much that is welcome to all practical men, over and above the completest and most carefully worked-out statistics ever published in that line."

Under the heading, "Raw Materials of Manufacture," we are informed that in February, 1902, sulphur was still being extracted by the Frasch process in Louisiana, at the rate of 100 tons per day, with a boiler capacity of 2100 horse-power, which was to be increased to 4300 horse-power. During the year 1900-1901 147,094 tons sulphur were exported to the United States from Sicily, 98,455 tons to France, 85,210 tons to Italy, and 30,549 tons to Germany; the total exports from Sicily were 521,497 tons. Much of the pyrites used comes from Spain and Portugal, where large deposits of rich ore, containing copper, are found. In Germany, Meggen pyrites, containing zinc, is used. [The zinc sulphate, contained in the ash, is sometimes extracted and used in the manufacture of lithophone.—Reviewer.] France produces most of its pyrites. Large deposits are found at Falun, Sweden, and in Norway. In the United States pyrites are found in New Hampshire, Massachusetts, New York, Virginia and Georgia.

Dr. Lunge appears not to have heard of the deposits of nitrate of soda in Death Valley, Cal., though a recent bulletin, by Bayley, estimates the total to be upwards of 22,000,000 tons. Under nitric acid manufacture it may be noted that nitric acid is only occasionally made for use in the manufacture of sulphuric acid. Generally it is made for the manufacture of mixed acids to be used in the nitroglycerin or nitrocellulose industry. The weak tailings so obtained, only, are used in the production of sulphuric acid. Dr. Lunge's treatment of this subject, therefore, is not altogether satisfactory. The object of the nitric acid manufacture, in nine cases out of ten, is to obtain the largest output, of greatest strength, lowest in oxides of nitrogen, in the smallest time, with the least plant and smallest fuel consumption. So great is the

demand for strong acid that at some works, as in those of the California Powder Co., at Pinole, Cal., the niter is melted before charging in order to drive off all the water. The introduction of the contact process for sulphuric acid will undoubtedly modify, to some extent, the position of the nitric acid producer.

Herreshoff's burner for pyrites fines is noticed in this edition for the first time, and a new plate illustrates the Rhenania zinc blende roaster. A brief description, without diagrams, is given of the Meyer tangent system of chambers, which the author considers a doubtful improvement. Additional information is given on the use of liquid water in place of steam; methods for the mechanical production of draught are also described. Herreshoff's modification of the Glover tower, one of the greatest of modern improvements, is dismissed in eight lines and no figure is given. His method of distributing the acid for this tower is not mentioned. One of the greatest improvements in concentration, that of L. Kessler, is fully described and illustrated.

The greatest interest will be felt by most readers in the description of the various contact processes, which contains a careful digest of the published and some unpublished information in 133 pages. This process bids fair to effect a complete revolution in sulphuric acid manufacture and to greatly modify many dependent industries, as it seems to be a cheaper method of manufacture than the chamber process.

Dr. Lunge could scarcely expect to add to his great reputation, but a careful examination of this new edition amply justifies the closing sentence of his preface: "But nobody can do more than is in his power, and such readers as know (or think they know) this or that thing better, and who may be inclined to sharp criticism, had best ask themselves the question whether *they* would come up to the ideal if they had to write such a book, and whether they cannot derive some valuable information even from this imperfect performance." EDWARD HART.

COSMETICS. A Handbook for the Manufacture, Employment and Testing of all Cosmetic Materials and Cosmetic Specialties. BY THEODOR KOLLER. Translated from the German by CHAS. SALTER. London: Scott, Greenwood & Co., No. 19 Ludgate Hill, E. C. 1902. New York: D. Van Nostrand Co. Price, $2.50 net.

ties. But it is not always possible to obtain a special book on such subjects as cosmetics. Those who *know*, as a rule, do not write; those who write, too often do not know. The mystery of secrecy prevails concerning ingredients, proportions and products. And yet, the cosmetic industry, in its various branches, covers an output of millions each year. The field is crying for the data given, judging from the flow of letters this reviewer receives, asking for formulae and subjects covered by it. This book, "Cosmetics," embraces perfumes, hair restorers, depilatories, antiseptic washes, soaps, hygienic and toilet, preparations for the skin, teeth, mouth, etc., etc. The method of treating them is not that of the empirical mixer, but of the experienced man who reasons. The origin and description of the various chemicals, matured products and compounds, tests for impurities, difficulties in compounding, and disadvantages as well as advantages of different processes, are systematically discussed. The coloring-matters of commerce, flavors, essences, ethereal oils and perfumes, the colognes, extracts, etc., etc., are instructively reviewed. This is a book to both read for general information and to refer to as necessity requires. The succinct information extended in the first 100 pages, concerning the ingredients of cosmetics, their purity, impurities, characters, etc., is more than worth the price of the volume. There are points in which we differ in some directions, but this is to be expected where secrecy has been the law, as with the substances this book covers. For example, after giving excellent cautionary advice concerning depilatories, and plainly stating that "depilatories produce exactly the same results as shaving, the after-growth of the hair being accelerated," the method of making sulphuretted quicklime depilatory is given. But it is not stated that the product will keep but a short time and needs be made fresh. Such criticisms as this, however, are carping in view of the general excellence of the book. It should be in the hands of druggists, of chemists concerned in technical and analytical work that involves its field, and of those interested in the effects and preparation of cosmetics. The thoughtful man of experience will be benefited, the rule-of-thumb man saved much needless wandering.

JOHN URI LLOYD.

THE MINERAL INDUSTRY. Its Statistics, Technology and Trade in the United States and Other Countries, to the End of 1902. Edited by J. STRUTHERS, PH.D. New York. The Engineering and Mining Journal: 1903. Large 8vo. 891 pp. Price, $5.00.

This publication is so well and favorably known and appreciated at home and abroad that it will be quite sufficient recommendation to say that the present volume (Vol. XI) fully lives up to the standard of its predecessors.

Of the features deserving particular mention, we may notice a 31-page article by Frederick H. Lewis on "The Mechanical Equipment of a Modern Portland Cement Plant," which is a valuable and timely article; J. B. C. Kershaw's review of "Progress in Electrochemistry and Electrometallurgy in 1902;" C. H. Fulton's "Review of the Cyanide Process in 1902;" Prof. Hoffman's 30-page article on "Recent Improvements in Lead Smelting;" W. R. Ingall's 15-pages on "Zinc;" R. H. Richards on "Ore Dressing;" W. Campbell on "Metallography;" J. A. Mathews on "Alloy Steels;" W. McDermott on the "Concentration of Ores by Oil;" and T. S. Rickards' 40-page treatise on the "Sampling and Estimation of Ores in a Mine." Besides these are the always-good reviews by other regular contributors, including much valuable work by the editor.

There are few of us who could afford to be without this welcome annual visitor, even if the volume cost several times its present moderate price. J. W. RICHARDS.

EVAPORATING, CONDENSING AND COOLING APPARATUS. Explanations, Formulæ and Tables for Use in Practice. BY E. HAUSBRAND. Translated from the second, revised German edition by A. C. WRIGHT, M.A, (Oxon), B.Sc. (Lond.). 21 illustrations and 76 tables. xxiii + 400 pp. London: Scott, Greenwood & Co.; New York: D. Van Nostrand Company. Price, $5.00.

This book fills a long-felt want of technical and manufacturing chemists in this country. Here, too often, the chemist must be his own engineer. Too often the education of chemists fails to cover the principles of mechanics and engineering so necessary to rational work. Experience is therefore frequently costly, even when the chemist has had the assistance of the professional engineer who, having limited knowledge of chemistry, fails to grasp the true needs of the situation. The author, in his preface, very rightly says: "The problems which are to be solved in the

construction of apparatus for evaporating, condensing and cooling are intimately connected with the laws of transfer of heat. Although, generally speaking, these laws are known, *yet reliable knowledge of the practical coefficient applicable in each of the many different cases is often wanting.*" The italics are ours. A great truth is here expressed and many who have had to struggle with the familiar difficulties, will thoroughly appreciate it and will heartily welcome the assistance this book will certainly afford. It is fortunate that one who has the knowledge and experience has also had the time and the will to make such splendidly systematic record of it. Every point in the practice seems to have been covered, and equations and tables are generously provided to enable one to work out his needs in each particular case. We heartily commend the book to the favorable attention of all working chemists, as well as to engineers who may be called upon to treat the problems it covers.

WM. MCMURTRIE.

THERMODYNAMICS AND CHEMISTRY. A non-mathematical treatise for chemists and students of chemistry. BY P. DUHEM. Translated from the French by G. K. BURGESS. New York: John Wiley & Sons. 1903. 8vo. 433 pp. Price, $4.00.

Professor Duhem's works on thermodynamics and chemical dynamics easily place him at the head of the French school in these subjects, and it is fortunate that English readers now have access to one of the most useful works of this author. A characteristic of this volume is the high appreciation which the author expresses for the work of J. Willard Gibbs; in fact, he goes to the extent of saying that this book is largely an exposition of ideas coming originally from America.

The work is admirably translated, and beautifully printed, with plenty of light and shade in the type used, so as to set out the headings and important paragraphs. The linotype machine is probably responsible for the frequent dropping out altogether of a letter, a freak which occurs so often as to become annoying to the reader.

To the student of chemistry who wishes to learn thermodynamics in the easiest manner possible, this work is recommended as probably meeting the requirements better than any English book heretofore published. J. W. RICHARDS.

LABORATORY EXPERIMENTS. For students in general chemistry in the University of Wisconsin. BY VICTOR LENHER. Second Edition. Madison, Wis.: Tracy, Gibbs & Co. 1903. pp. 31. Price, 50 cents.

The experiments prescribed begin with exercises upon glass bending and cutting, and upon chemical and physical change, after which the elements are taken up in the following order: hydrogen, chlorine, oxygen, nitrogen, carbon, the halogens, sulphur, the phosphorus group, silicon, boron, the alkalies, the alkaline earths, magnesium, zinc, cadmium, mercury, copper, silver, tin, lead, nickel, cobalt, iron, aluminum, chromium, and manganese. The treatment is essentially qualitative, although a few quantitative experiments have been introduced.

The manual contains no prefatory statements, but is presumably prepared to accompany the author's lecture and classroom instruction, and can, therefore, hardly be judged by itself. It contains little or nothing which can be regarded as unique, but the student who has conscientiously completed the experiments as prescribed, and given the explanations asked for, should have acquired a considerable knowledge of descriptive chemistry and a useful training in accurate observation.

The alternate (right-hand) pages of the book are blank; the typography leaves something to be desired. H. P. TALBOT.

A MANUAL OF QUALITATIVE CHEMICAL ANALYSIS. BY J. F. MCGREGORY. Boston: Ginn & Co. 1903. 133 pp. Price, $1.10.

The book is divided into four parts. Part I gives the usual reactions of the common metals and acids. Part II describes blowpipe analysis very briefly. Part III takes up systematic methods for the metals and acids in solution. Part IV is devoted to the examination of "complex" solids. The author makes no use of the modern theory of solution, stating in the preface: "That however valuable the study of this subject may be to the chemist, its introduction as a basis of study in qualitative analysis is not to be recommended." On looking through the book, nothing new or original is to be found, unless $(NH_4)_3PO_4(MoO_3)_{10}$ as the formula of ammonium phosphomolybdate and some other errors should be so considered.

As the reviewer believes that qualitative analysis should be taught from the standpoint of reactions of ions, this book does not appeal favorably to him, and the question, which naturally

suggests itself when a new book on qualitative analysis appears—why was this published?—remains without an answer.

E. H. M.

A LABORATORY GUIDE TO QUALITATIVE ANALYSIS WITH THE BLOWPIPE. By F. W. MARTIN, PH.D. New York: John Wiley & Sons. 1903. 12mo. iv + 41 pp. Price, 60 cents net.

The author of this little book states that, in his judgment, the restricted use of blowpipe methods as a means of qualitative analysis is due mainly to the lack of a manual on the subject which is designed specifically for the analysis of compounds in general. To meet this deficiency he has arranged a scheme of analysis which is the feature of the book and which consists of well-known tests applied in the following order: 1, Closed tube; 2, open tube; 3, on plaster tablet, (*a*) *per se*, (*b*) with hydriodic acid, (*c*) with hydrobromic acid, (*d*) with stannic chloride, (*e*) with cobalt nitrate; 4, flame reaction; 5, bead reactions; 6, sodium carbonate on charcoal; 7, zinc and hydrochloric acid, after fusion with sodium carbonate and potassium nitrate; 8, fusion with acid potassium sulphate or sodium carbonate for detection of acids. Excellent cross references add greatly to the value of the scheme.

While the reviewer can not agree with the opinion of the author, as stated above, it is undoubtedly true that many substances, especially those of a simple nature, can be advantageously ana- especialy those of a simple nature, can be advantageously analyzed by the scheme presented. It is doubtful, however, if the book will recommended. Very little attention is paid to the greatest difficulty of its use, *i. e.*, interfering elements and their separation. Some of the tests given cannot be relied upon except for the purest material, and a few are insufficient for identification even when free from admixture. The blowpipe has its use, but too much has often been claimed for it, even in the hands of the expert. A few important blowpipe reactions have been omitted, such as the coatings obtainable on charcoal and the metallic buttons which are so easily produced by means of sodium from many compounds and ores, and even from the silicates of the malleable metals. The manual is without cuts of any kind and assumes the guiding hand of a teacher already familiar with the subject. For class use this has, perhaps, a distinct advantage, as cumbrous details are omitted.

Taken as a whole, the book is one of the best short manuals of blowpiping to be had. It will scarcely be adopted as a means for general qualitative analysis, but it is well worth the price asked, for use in the blowpipe laboratory or even as an adjunct to a qualitative course. It is well printed, well indexed and contains few errors. CHARLES L. PARSONS.

CORRECTION.

In the paper by W. Geo. Waring on "The Volumetric Determination of Zinc," page 29, the factors for zinc ammonium phosphate and zinc pyrophosphate should be, respectively, 36.64 and 42.91 instead of 37.28 and 42.77, as given.

nuals
neans
price
junct
con-
NS.

Deter-
phos-
4 and